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CHELATE WATER SOLUTION LASERS

FINAL TECHNICAL SUMMARY REPORT

1 July 1964 - 31 December 1964

E. P. Riedel

R. G. Charles

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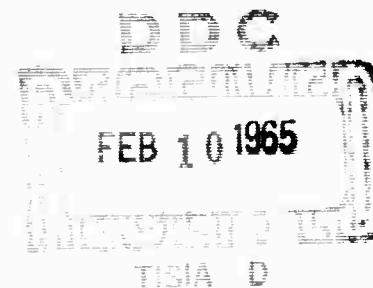
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WESTINGHOUSE RESEARCH LABORATORIES

Pittsburgh, Pennsylvania 15235

Contract No. Nonr-4573(00)

ARPA Order No. 306



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E. P. Riedel

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ABSTRACT

Heavy water is considered as a liquid laser solvent. Its unique combination of good optical homogeneity, low absorption at the laser output frequency and low viscosity make it very attractive for proposed high radiance liquid laser systems.

The heavy water soluble rare-earth chelate research at the Westinghouse Research Laboratories both before the start and during the present contract is described. Chelates having adequate solubility, high quantum efficiency and improved absorption bands have been developed. Unfortunately, photodecomposition of these chelates has prevented laser action from being achieved. It is expected, however, that this problem can be overcome.

The work with europium benzoyltrifluoroacetate both before and after the end of the present contract is described. To date, laser action has been achieved in 10 salts of this compound in acetonitrile near room temperature. Output beam divergence, spectral narrowing and thresholds for laser action are discussed.

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1. Introduction

Since 1961 Westinghouse has been engaged in liquid laser research. Government-sponsored work in this field did not, however, begin at Westinghouse until the start of the present contract, i.e., July 1, 1964.

All of the work summarized in Section 2 was done before July 1, 1964. Section 2 describes work done with rare earth chelates dissolved in both organic solvents and in heavy water. Also included in Section 2 is a description of some of the potential advantages of heavy water over known organic solvents for use in liquid laser systems. Section 2 is intended as a general technical background for the work done under the present contract which is described almost entirely in Section 3.

Section 3 summarizes studies of rare earth chelates soluble in heavy water.

Some of the work presented in Section 4 was completed before the end of the present report period which was December 31, 1964. The remainder of the work described in Section 4 was completed after December 31. Section 4 describes work done with a number of salts of europium benzoyl-trifluoroacetate dissolved in acetonitrile including successful laser operation at and near room temperature. This work has been included in this report because of its general implications concerning the feasibility and potential advantages to be gained with a heavy water laser system.

2. Technical Summary of Work Done at Westinghouse Before the Start of the Present Contract

2.1 Rare Earth Chelate Work in Organic Solvents

The early work of Weissman⁽¹⁾ with rare earth chelates in organic solvents showing characteristic narrow-line fluorescence of rare earth ions led to the consideration of rare earth chelates as potential laser materials. In order to obtain more information concerning the potential value of chelates for laser applications europium trisdibenzoylmethide, $\text{Eu}(\text{DBM})_3$, was synthesized and its absorption and fluorescent properties studied in ten different organic solvents.⁽²⁾ A considerable amount of information concerning the spectroscopic properties of the chelate was obtained.

In agreement with the earlier work of Weissman⁽¹⁾ and Cosby,⁽³⁾ characteristic europium ion emission was observed when light was absorbed by the organic complex surrounding the europium ion. It was shown that 5% of the emitted quanta appeared in the transition from the $^5\text{D}_0$ to the ligand-field-split $^7\text{F}_2$ states. Since the $^7\text{F}_2$ states were high enough above the ground level (about 900 cm^{-1}) to be essentially unpopulated even at room temperature, the material was considered as a 4-level laser system.⁽²⁾ The fluorescent quantum efficiency and the fluorescent decay time of the principal emission line were measured as functions of temperature and solvent. Decay times of the order of a few hundred microseconds were observed. Quantum efficiencies near one were observed at low

temperatures, and it was also shown that the quantum efficiency was independent of exciting wavelength within the absorption band. A consideration of the important general problems of the very intense chelate absorption band and scattering due to index of refraction variations during flash excitation was also given in calculating the expected laser threshold. These problems will be discussed in the following sections. In fact much of the work described in this report has been aimed at solving these two problems. Unfortunately, as will be discussed in Section 4, both of these problems are still unsolved, even in the liquids which are at room temperature.

Additional studies at the Westinghouse Research Laboratories of the properties of europium dibenzoylmethide and its complexes with Lewis bases, ⁽⁴⁻⁷⁾ rare earth salicylaldehyde chelates ⁽⁸⁾ and europium thenoyltrifluoroacetate ⁽⁹⁾ have served to add to the general knowledge of rare earth chelate properties.

2.2 Time Dependent Scattering

The creation of refractive index gradients within a laser material during the optical pumping process can be an important deleterious effect on laser performance. When a laser material is optically pumped, its temperature changes since part of the pump energy is dissipated in the material. If this energy is dissipated nonuniformly within the material, which in practice is always the case, thermal gradients will exist within the material. Since almost all known materials have non-zero coefficients of refractive index change with respect to temperature (dn/dT), refractive index gradients result. Refractive index gradients will cause scattering losses within the optical cavity. These losses will raise the threshold of the laser. In

addition, it seems reasonable to expect that scattering within the laser cavity will also tend to increase the output beam divergence above the diffraction limit.

The value of dn/dT in all organic solvents for which data are available near room temperature is about $4 \times 10^{-4}/^{\circ}\text{C}$. This is much larger than typical values for crystals. For example, the value of dn/dT for sapphire is $1.26 \times 10^{-5}/^{\circ}\text{C}$ at 7065 Å.⁽¹⁰⁾

In order to ascertain the importance of the comparatively large value of dn/dT of organic solvents for use in proposed low-viscosity liquid laser systems near room temperature, a series of experiments were performed at Westinghouse. These experiments⁽¹¹⁾ measured the time dependent scattering of a collimated gas-laser beam of light (6328 Å) while traversing the laser material during flash excitation. The result obtained for a 3:1 ethanol-methanol mixture with a europium chelate in solution at room temperature showed that the diffraction limited gas-laser beam divergence angle of about 4×10^{-4} radians was broadened to greater than 10^{-2} radians in traversing 8 centimeters of the solution during the flash.⁽¹¹⁾ It was concluded therefore that the comparatively high scattering would raise the threshold⁽¹¹⁾ for laser action for liquid lasers using organic solvents near room temperature. In addition, it seemed reasonable to expect that the severe scattering would also tend to increase the output beam divergence considerably above the diffraction limit.

2.3 Heavy Water as a Liquid Laser Solvent

The severe light scattering observed in organic solvents during optical pumping experiments⁽¹¹⁾ has led to the consideration of heavy water as a preferred solvent for liquid laser work.⁽¹²⁾

This is because the only pure solvents which are known to have small values of dn/dT at temperatures where their viscosities are low are water and heavy water. In fact, the refractive index versus temperature curves for water and heavy water display maxima ($dn/dT = 0$) at about -1.5 and $+6^{\circ}\text{C}$, respectively.⁽¹³⁾ Some of the data on water and heavy water in Ref. 13 are shown in Fig. 1. For purposes of comparison, data for methanol, a typical organic solvent, and for sapphire are also shown in Fig. 1.

The data in Table III on p. 164 of Ref. 13 indicate that for a mol fraction of $\text{D}_2\text{O} = 0.977$, the index changes by 1×10^{-5} between temperatures 3.1 and 7.5°C at 6563 \AA . The value of dn/dT near room temperature for sapphire is $1.26 \times 10^{-5}/^{\circ}\text{C}$ at 7065 \AA . For a temperature change of 4.4°C near room temperature for sapphire, the total change in index Δn would be $4.4 (1.26 \times 10^{-5}) = 5.5 \times 10^{-5}$, at $\lambda = 7065 \text{ \AA}$. Thus for a temperature change of 4.4°C near 5°C , the change in index is about 5 times smaller for heavy water than for an equal temperature change near room temperature for sapphire. These results are combined with similar results for methanol and summarized in Table I.

Table I

Total Index of Refraction Change for Heavy Water, Methanol, and Sapphire

Material	Wavelength (\AA)	Temperature Range	Temperature Change	Index Change
D_2O	6563	3.1 to 7.5°C	4.4°C	1×10^{-5}
Sapphire	7065	20 to 24.4°C	4.4°C	5.5×10^{-5}
Methanol	6563	20 to 24.4°C	4.4°C	180×10^{-5}

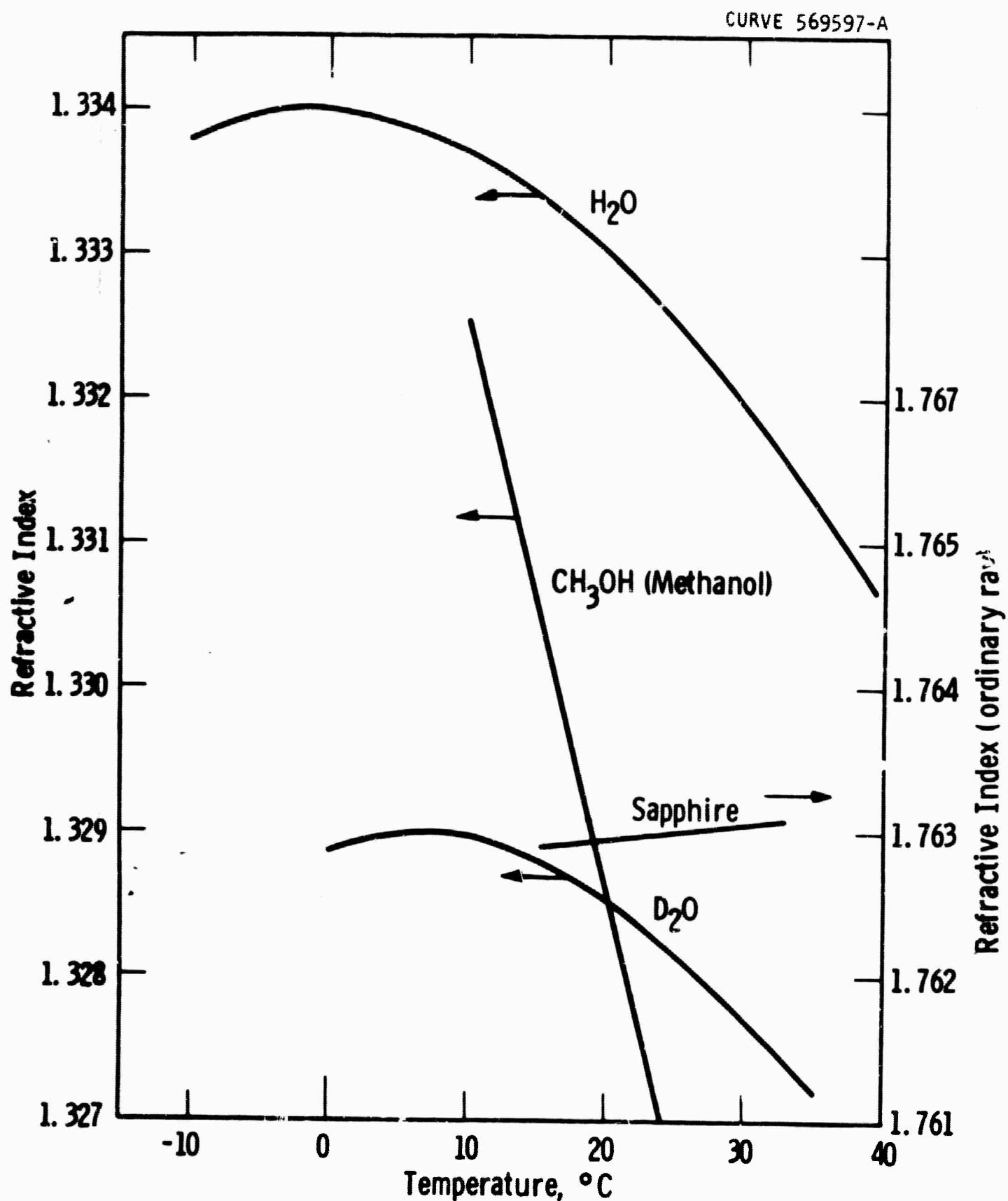


Fig. 1—The refractive index vs temperature of water, heavy water, methanol and sapphire

Scattering experiments at Westinghouse using europium chelates in D_2O at $5^\circ C$ similar to those described in Section 2.2 show much less scattering than in the 3:1 ethanol-methanol solution.

Calculations show that the temperature rise may be kept below $4^\circ C$ for D_2O near $5^\circ C$, even for high pulse power operation without circulation, provided proper flash radiation filtering techniques and an active material with a reasonably high fluorescent quantum efficiency are used. For high repetition rate pulsed power or high power c-w operation, circulation of the D_2O solution between stationary ends forming the optical cavity and then cooling the solution in a different part of the cycle would be a practical way of solving the temperature rise problem.

Heavy water (D_2O) is to be greatly preferred over ordinary water for three important reasons:

1. Water must be supercooled to reach $-1.5^\circ C$, whereas heavy water freezes below $+6^\circ C$ (at about $+3.8^\circ C$).
2. The fluorescent quantum efficiency for some rare earth compounds is higher in D_2O than in water⁽¹⁴⁾ (see also Section 3.1).
3. The absorption at the laser wavelength (near 6120 Å for Eu^{+3}) is lower in D_2O than in water. The measured absorption coefficient⁽¹⁵⁾ for heavy water at 6120 Å is $4.3 \times 10^{-4} \text{ cm}^{-1}$ while that for H_2O is $29.6 \times 10^{-4} \text{ cm}^{-1}$. The eventual utilization of long lengths of D_2O liquid laser solutions is made possible by the extremely small value of the absorption coefficient.

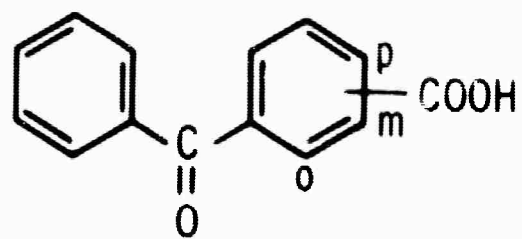
2.4 Early Work with Rare Earth Chelates Soluble in Heavy Water

Since the studies just described predicted that heavy water should have significant advantages as a liquid laser host, the liquid laser work

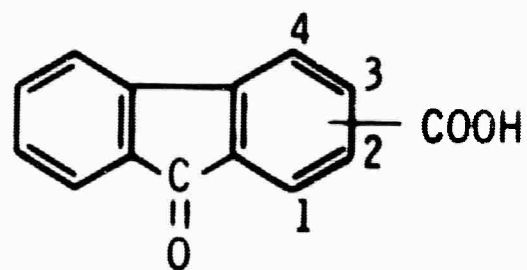
at the Westinghouse Research Laboratories has consequently emphasized research on systems which will be capable of laser oscillations in heavy water solution.

The best known class of rare earth chelates which has both adequate water solubility and high stability toward dissociation in solution consists of chelates derived from aminopolycarboxylic acids. Examples of such chelates which were studied at Westinghouse before the start of the present contract are europium and terbium ethylenediamine-tetraacetate (EuEDTA and TbEDTA) and europium and terbium diethylene triamine pentaacetate (EuDETA and TbDETA). Representative diagrams of these compounds are shown in Figs. 2 and 3.

The absorption, emission spectra, and decay times of EuDETA and TbDETA are shown in Figs. 4 through 9. All of the materials show bright line fluorescence characteristic of the trivalent rare earth ion. The absorption spectra of these chelates all show bands in the ultraviolet with wings extending toward the blue to 3500 Å in some cases. These bands are due to the organic part of the chelate. At high concentration, absorption spectra characteristic of the rare earth ions themselves have been observed. For example, the absorption near 4000 Å in Fig. 4 and 3500 Å in Fig. 7 is due to transitions from the ground level to excited states of Eu^{+3} and Tb^{+3} , respectively. The molar absorption coefficient, ϵ , for pink ruby is about 40 near the peak of the absorption band in the green.⁽¹⁶⁾ This is a desirable value of ϵ for many practical optical pumping conditions. We see, therefore, that the absorption transitions due to Eu^{+3} and Tb^{+3} are not very satisfactory for purposes of laser pumping since they are too weak and also quite narrow. Excitation of these chelates in the organic



Benzoylbenzoic
Acids



Fluorenone Carboxylic
Acids

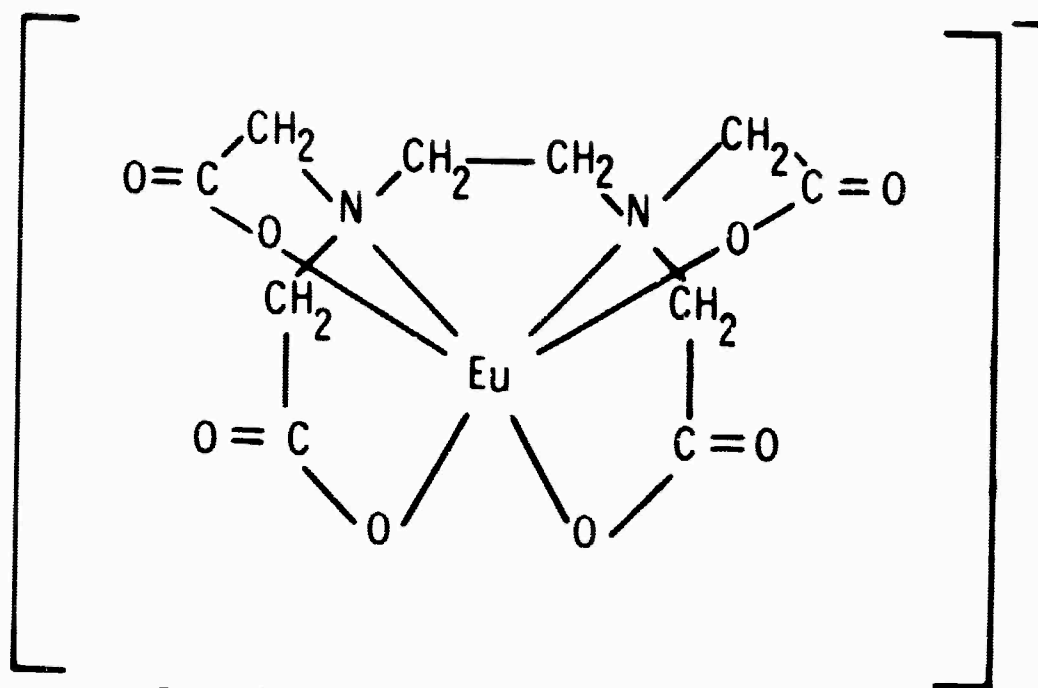
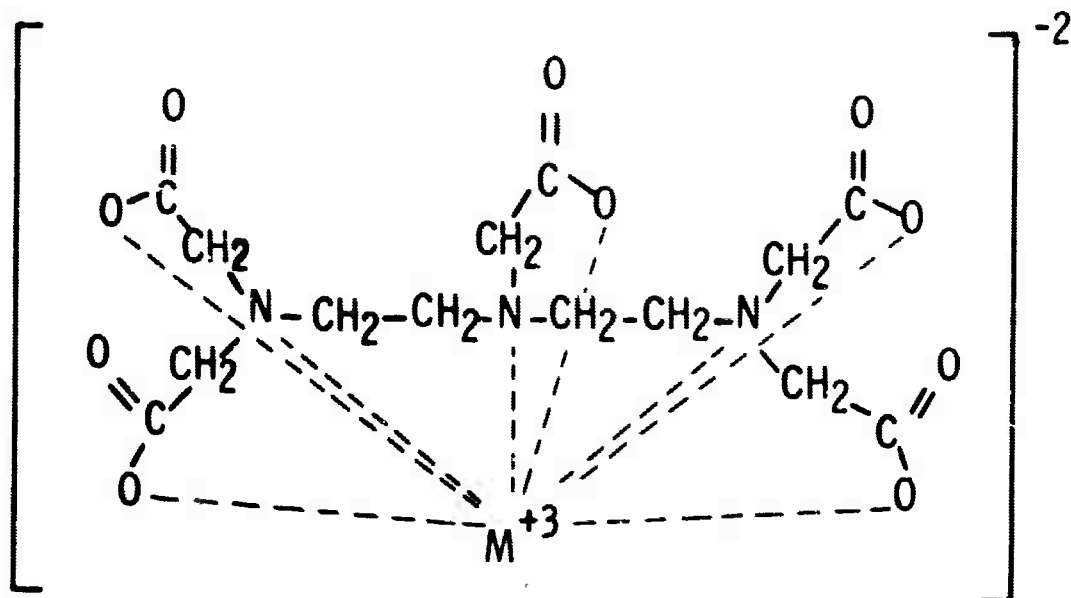


Fig. 2 Europium Ethylenediaminetetraacetate



Metal (III) diethylene triamine pentaacetate ion

Fig. 3

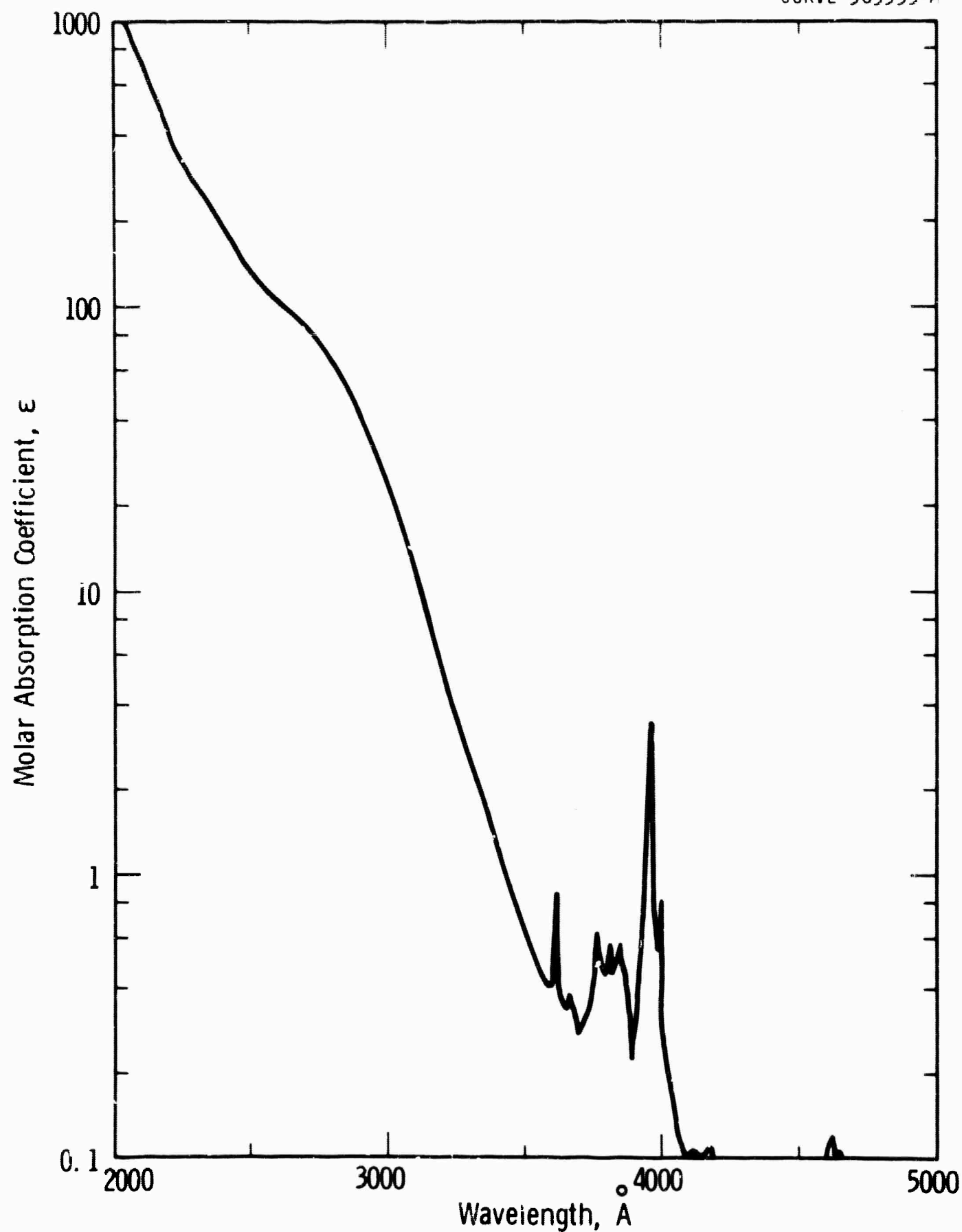


Fig. 4—Absorption spectrum Na_2Eu diethylene triamine pentaacetate in D_2O at 300°K

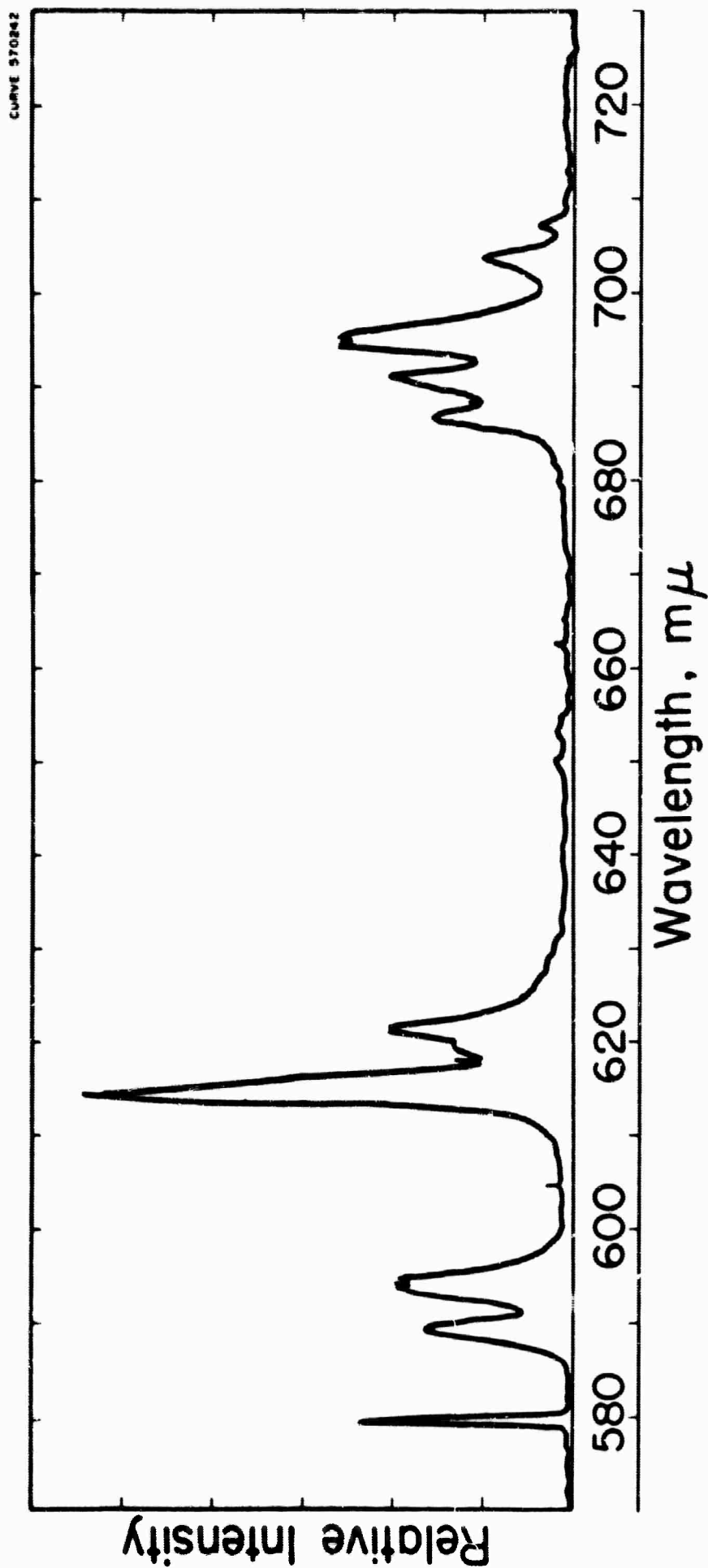
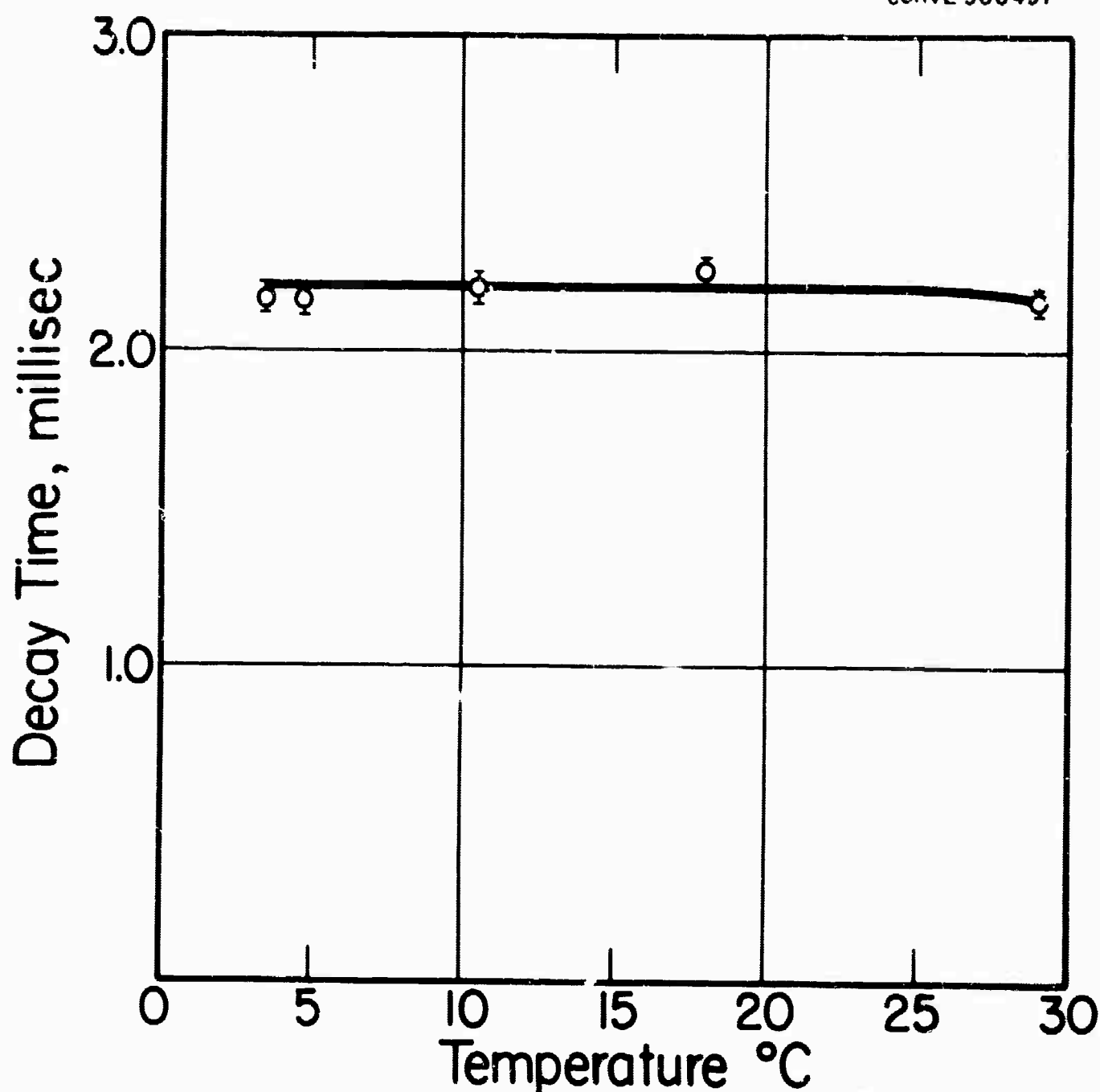


Fig. 5 Fluorescence spectrum of sodium europium diethylene triamine pentaacetate in heavy water (0.036M), 300°K, near UV excitation $\frac{48}{48}$ resolution.



Measured decay time of the 5D_0 level of Eu^{+3} in the Eu(III) diethylene triamine pentaacetate ion in D_2O versus temperature:

Fig. 6

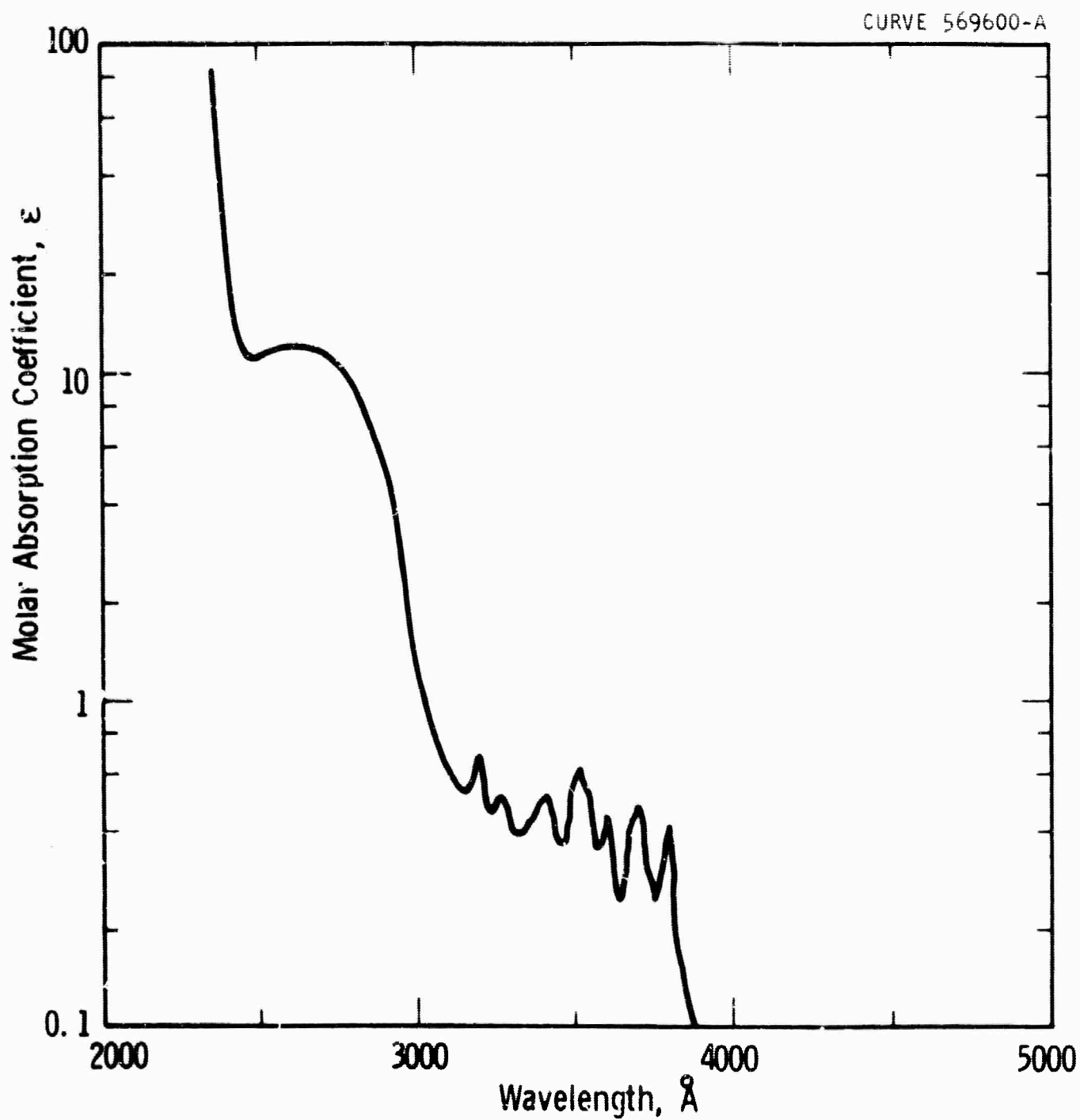


Fig. 7 Absorption spectrum Na_2Tb diethylene triamine pentaacetate in D_2O at 300°K

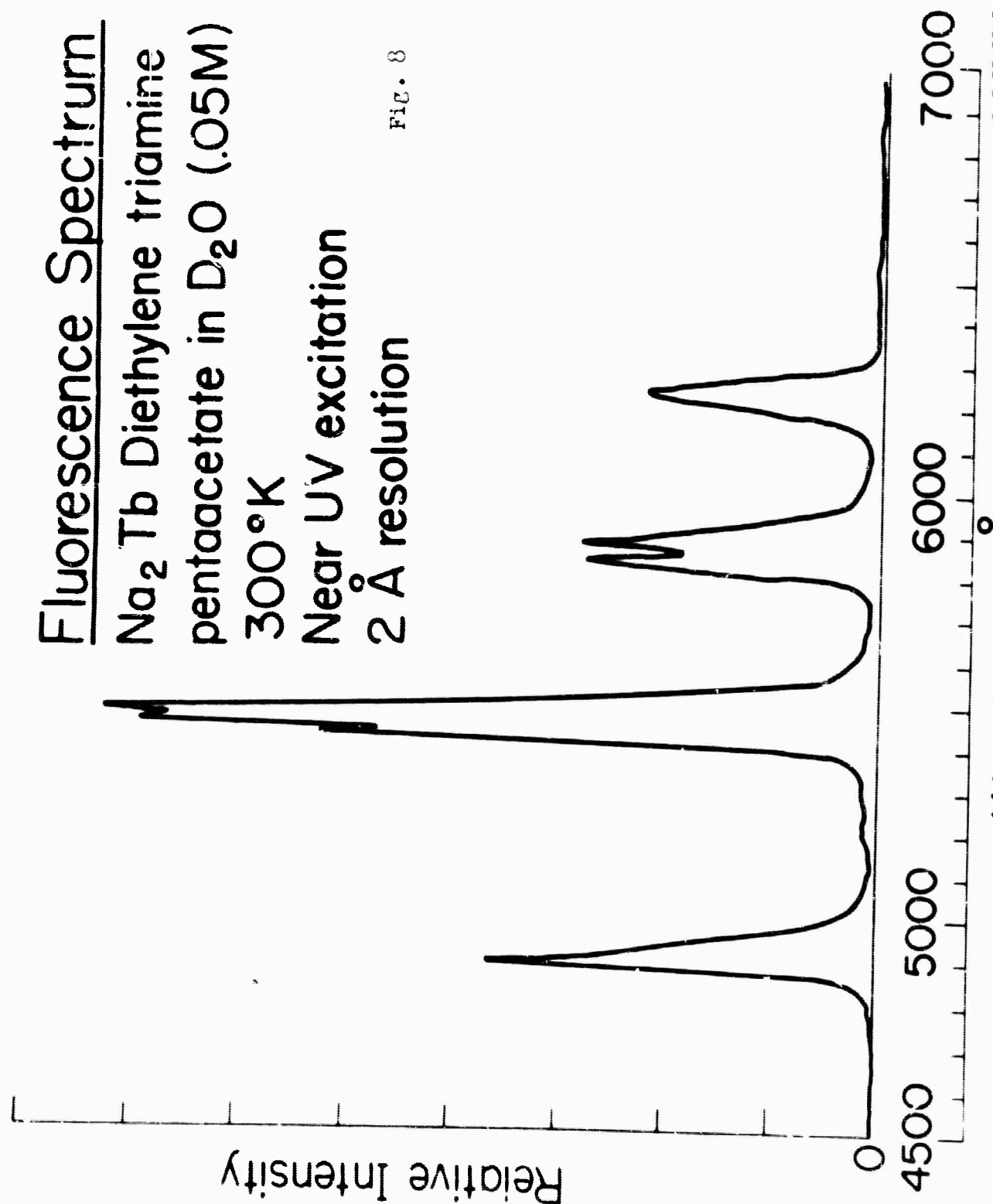
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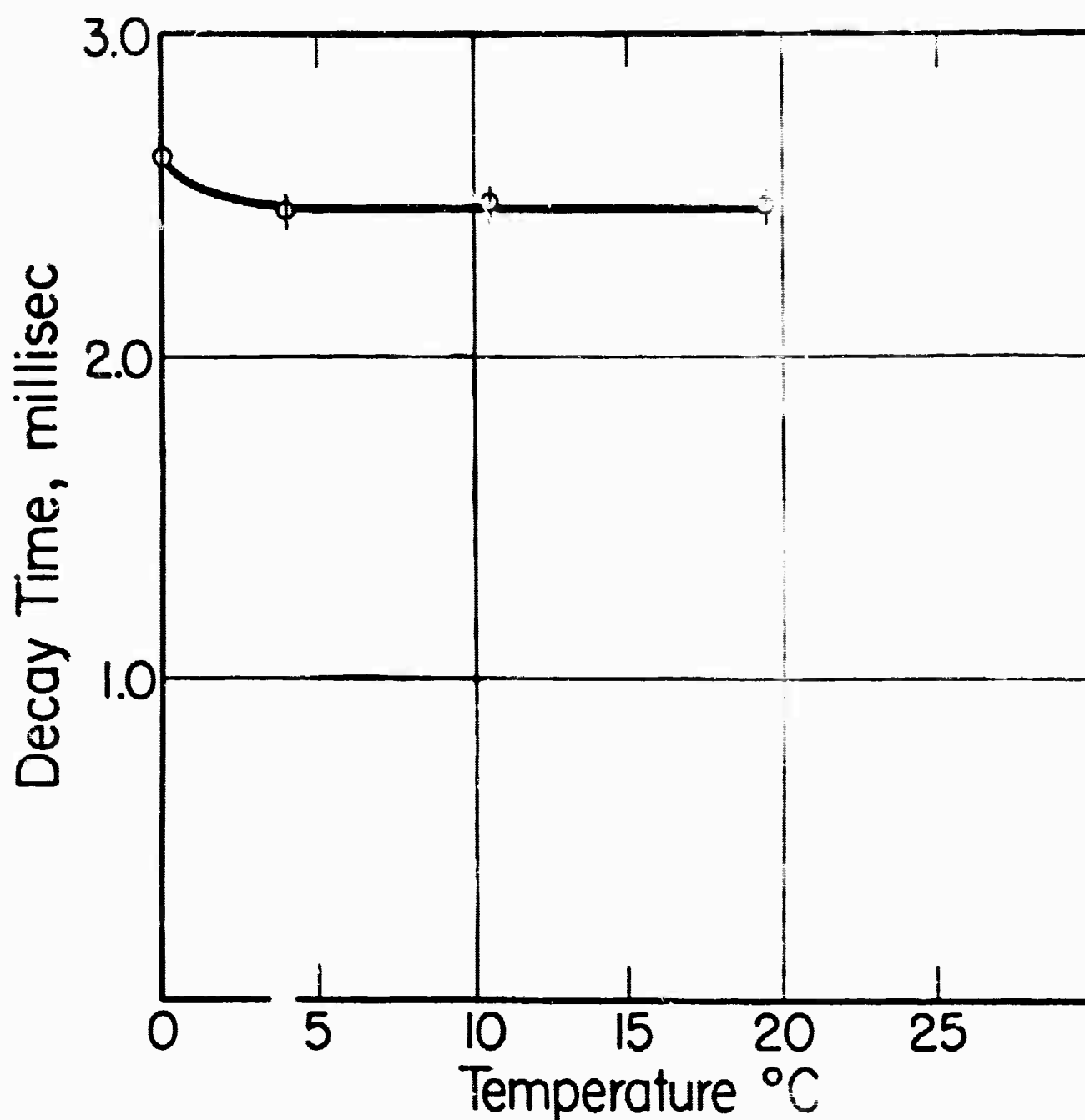
Fluorescence Spectrum

Na₂Tb Diethylene triamine
pentaacetate in D₂O (.05M)
300°K

Near UV excitation
2 Å resolution

Fig. 8





Measured decay time of the 5D_4 level of Tb^{+3} in the $Tb(III)$ diethylene triamine pentaacetate ion in D_2O versus temperature.

FIG. 9

part of the absorption band at 2537 Å is, however, not effective in exciting rare earth ion fluorescence indicating that transfer of energy from the ligands does not take place to the rare earth ion. Therefore, for these chelates the observed fluorescence is due to direct excitation of the rare earth ion.

The poor overall absorption characteristics of these compounds therefore make them unattractive from the standpoint of laser materials.

3. Chelates Soluble in Heavy Water

In order to develop chelates with more suitable absorption properties for optical pumping purposes than those described in Section 2, the work discussed in Section 3 was performed. The studies described in Sections 3.1 and 3.3 were begun with Westinghouse funds. This work was finished under the present contract. The studies summarized in 3.2 were performed under the present contract.

3.1 Mixed Ligand Complex Formation Between Europium Ethylenediaminetetraacetate and p-benzoylbenzoate

The system described in this section does not lose because of photodecomposition of the chelate. However, the system is important in that it represents the first successful incorporation of a comparatively broad absorption band of moderate intensity in a rare earth system which fluoresces with high quantum efficiency in D_2O at room temperature. In addition, it is reasonable to expect that photodecomposition in related systems can be avoided. Fundamental work in the general area of photodecomposition of chelates is, however, badly needed.

The best known class of rare earth chelates which has both adequate water solubility and high stability toward dissociation in solution consists of chelates derived from aminopolycarboxylic acids such as EuEDTA and EuDETA (see Figs. 2 and 3). As indicated in Section 2.4 however, such chelates do not, in general, have sufficient

optical absorption in the near ultraviolet for efficient utilization of pump light. For this reason we have investigated the properties of mixed ligand rare earth complexes derived from aminopolycarboxylate ions and a second complexing agent which absorbs in the near ultraviolet. We describe here a study of mixed ligand complex formation between Eu^{+3} , the ethylenediaminetetraacetate anion (EDTA^{4-}) and the p-benzoylbenzoate anion (BB^-) in H_2O and D_2O . The anion EuEDTA^- is shown at the bottom of Fig. 2. If the COOH group is attached to the p position in the diagram at the top left of Fig. 2 and the hydrogen ion removed, the anion remaining is (BB^-).

The p-benzoylbenzoate anion was chosen because of its favorable absorption band (as discussed below) in the near ultraviolet.

Nature of Species Formed

When heavy water solutions containing EuEDTA^- and BB^- are illuminated with ultraviolet light, much brighter orange-red fluorescence is observed than for an equally concentrated solution of EuEDTA^- alone. This section outlines evidence for mixed ligand complex formation involving both anions.

When EuEDTA^- and BB^- are combined in water solution at low values of the ratio of concentrations $\text{BB}^-_{\text{total}}/\text{EuEDTA}^-_{\text{total}}$ a portion of the europium is precipitated (Curve A, Fig. 10). As the relative amount of BB^- is increased, the precipitate redissolves; and above a ratio of about 6 a clear solution is obtained. Elemental analysis of the precipitate obtained at low values of $\text{BB}^-_{\text{total}}/\text{EuEDTA}^-_{\text{total}}$ shows

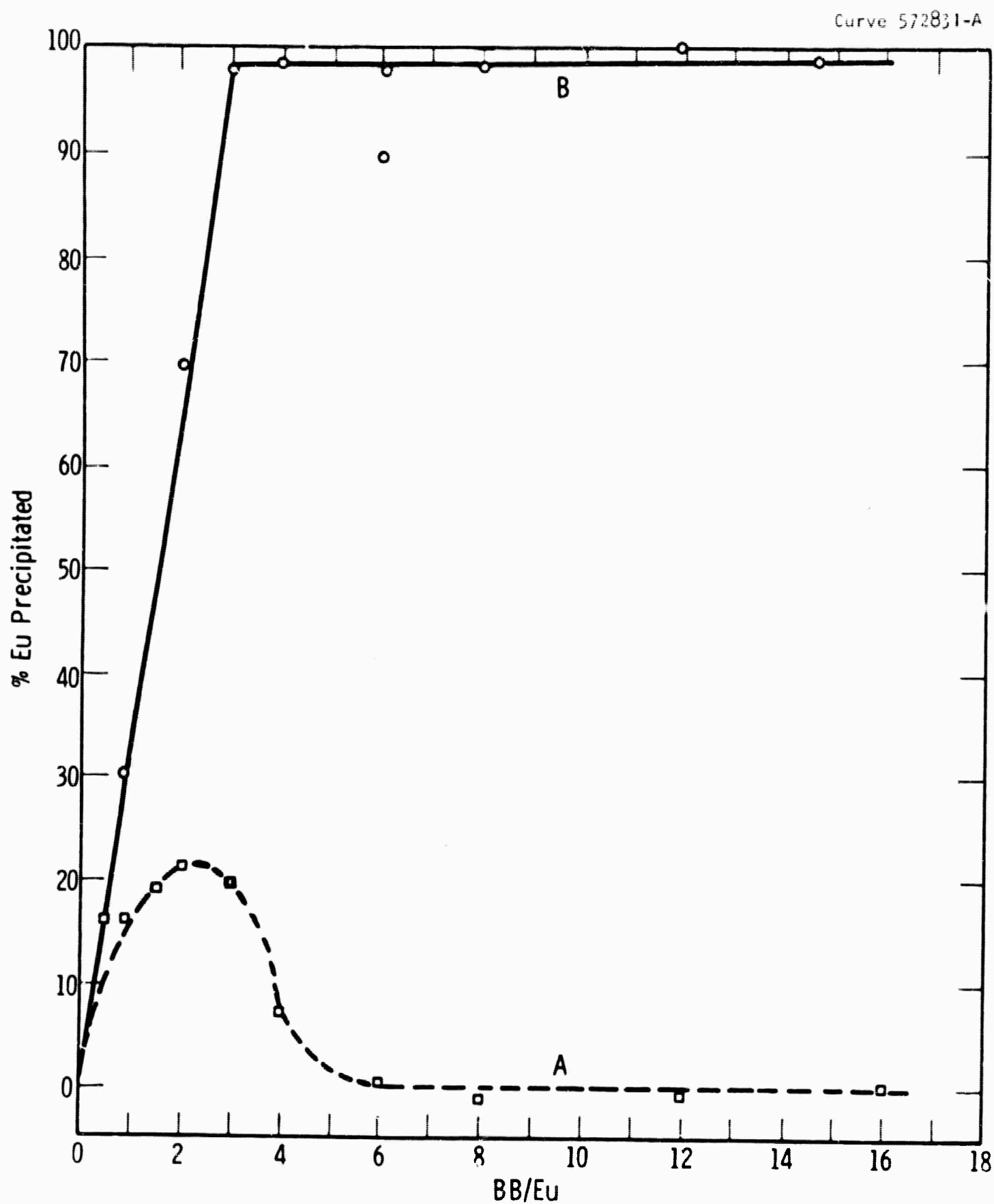
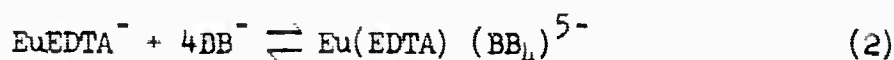
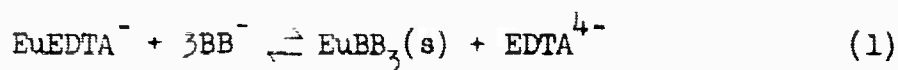


Fig. 10. Fraction of total europium precipitated by sodium p-benzoylbenzoate from solutions containing (A) NaEuEDTA or (B) EuCl_3 .

the precipitate to be nitrogen-free and the composition corresponds to that of hydrated EuBB_3 .

Curve A of Fig. 10 is explainable in terms of the competing equilibria 1 and 2.



Displacement of EDTA^{4-} from the very stable complex EuEDTA^- by BB^- (Eq. 1) is rather surprising but is evidently associated with the low solubility of EuBB_3 in water.

That mixed ligand complex formation involving EDTA^{4-} occurs at the higher values of $\text{BB}^-_{\text{total}}/\text{EuEDTA}^-_{\text{total}}$ is shown by Curve B, Fig. 10. Addition of BB^- to Eu^{3+} , in the absence of EDTA^{4-} , results in nearly quantitative precipitation of the europium at $\text{BB}^-_{\text{total}}/\text{Eu}_{\text{total}} = 3$. There is no evidence for redissolution of the EuBB_3 at higher values of this ratio due to the formation of such species as EuBB_4^- . The precipitation of the europium as hydrated EuBB_3 in Curve A (Fig. 10) is further substantiated by the independent preparation and characterization of the salt $\text{EuBB}_3 \cdot \text{H}_2\text{O}$. (See Experimental Section.)

Fluorescence and Light Absorption Properties

Fig. 11 gives the fluorescence spectrum of a D_2O solution containing excess BB^- (to suppress precipitation of EuBB_3). The fluorescence is found to be due entirely to transitions within the 4 f shell of the bonded Eu^{3+} ion and the spectrum is similar to that obtained with other $\text{Eu}(\text{III})$ chelates (dissolved in organic solvents).^(2,17)

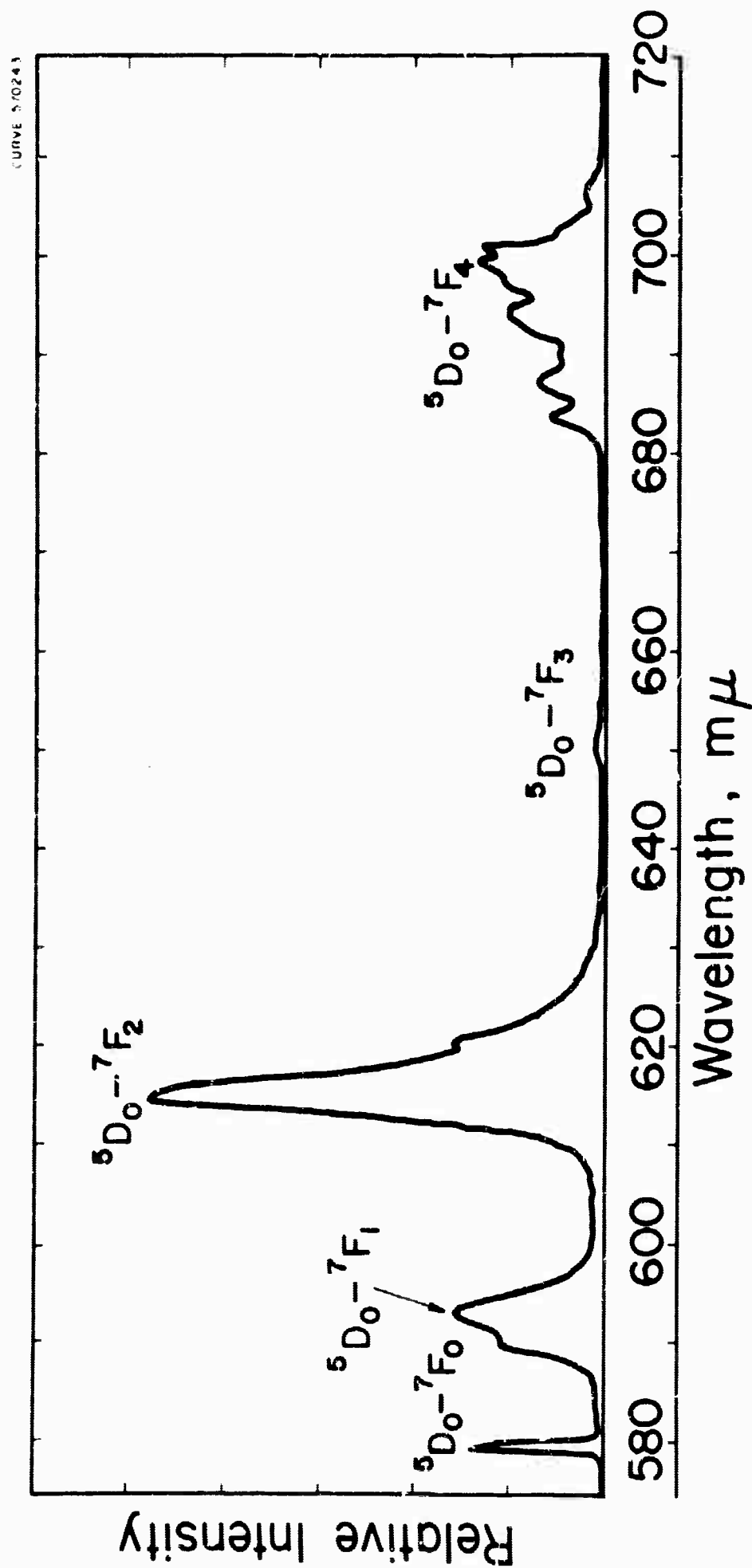


Fig. 11 - Fluorescence Spectrum of Sodium Europium Ethylenediaminetetraacetate (0.01M) + Sodium p-Benzoylbenzoate (0.2 M) in heavy water, 300°K, near UV Excitation and 4 Å Resolution

Transitions probably responsible for the observed groups of emission lines are indicated in Fig. 11. The fluorescence spectrum of EuEDTA^- alone in D_2O was also obtained. Except for greatly decreased overall fluorescent intensity (due at least in part to lower absorption of ultraviolet radiation) the spectrum was essentially identical to Fig. 11. The fluorescence spectrum of Eu^{3+} in chelates is known to be affected measurably by the formation of mixed ligand complexes.^(5,6) In the present instance it appears that there must be little change in the local environment of the Eu atom in $\text{Eu}(\text{EDTA})(\text{BB})_4^{5-}$ as compared with that in EuEDTA^- itself in solution.

While the structure of the EuEDTA^- ion in solution is not known, recently reported⁽¹⁸⁾ x-ray structural results for the crystalline chelates $\text{HLaEDTA} \cdot 7\text{H}_2\text{O}$ and $\text{KLaEDTA} \cdot 8\text{H}_2\text{O}$ are pertinent to the present discussion. Hoard and co-workers⁽¹⁸⁾ were able to show that the four oxygens and two nitrogens of EDTA were bonded to La in both compounds. In addition, four water molecules were bonded directly to La in $\text{HLaEDTA} \cdot 7\text{H}_2\text{O}$ and three in $\text{KLaEDTA} \cdot 8\text{H}_2\text{O}$ to give, respectively, coordination numbers of 10 and 9 for the lanthanum in the two compounds. Less complete x-ray data by the same authors indicate the EDTA complexes of other rare earths have similar structures. It seems probable, therefore, that the EuEDTA^- ion in solution has at least three water molecules bonded directly to the europium atom. Reaction with BB^- most probably involves displacement of these water molecules (and possibly also one of the EDTA carboxylate groups). Such displacement does not drastically change the nature of the atoms directly bonded to

the europium, and also need not change the local symmetry about the europium atom.

The relative fluorescence was measured of a series of solutions prepared from a constant amount of BB^- and varying amounts of EuEDTA^- . The results are shown in Fig. 12. The data can be represented by two straight lines. The rather ill-defined intersection at $[\text{EuEDTA}_{\text{total}}/\text{BB}_{\text{total}}] = 0.25$ is consistent with the formation of $\text{Eu}(\text{EDTA})(\text{BB})_4^{5-}$ as the principal fluorescent species.

The quantum efficiency was measured of a D_2O solution 0.2M in BB^- and 0.01M in EuEDTA^- . The value obtained of 15% is similar to those reported for certain of the europium β -diketone chelates in organic solvents at room temperature.^(2,17,19) The fluorescence was found to decay exponentially with a decay time of 2.0 msec. When H_2O was substituted for D_2O the fluorescence efficiency dropped to 2%. Kropp and Windsor⁽¹⁴⁾ have noted a similar enhancement of fluorescence for simple rare earth salts in D_2O as compared to H_2O . For both H_2O and D_2O the quantum efficiency of the present system was practically independent of temperature in the range 5° to 26°C .

The observed quantum efficiency was found to be measurably sensitive to the presence of dissolved O_2 . When the above air-equilibrated solution in D_2O was flushed with argon for 1/2 hr the quantum efficiency increased to 21%. When flushed with pure oxygen the efficiency decreased to 5%.

Absorption spectra are given in Fig. 13 for EuEDTA^- and for BB^- . It is apparent that for solutions containing both ions, in

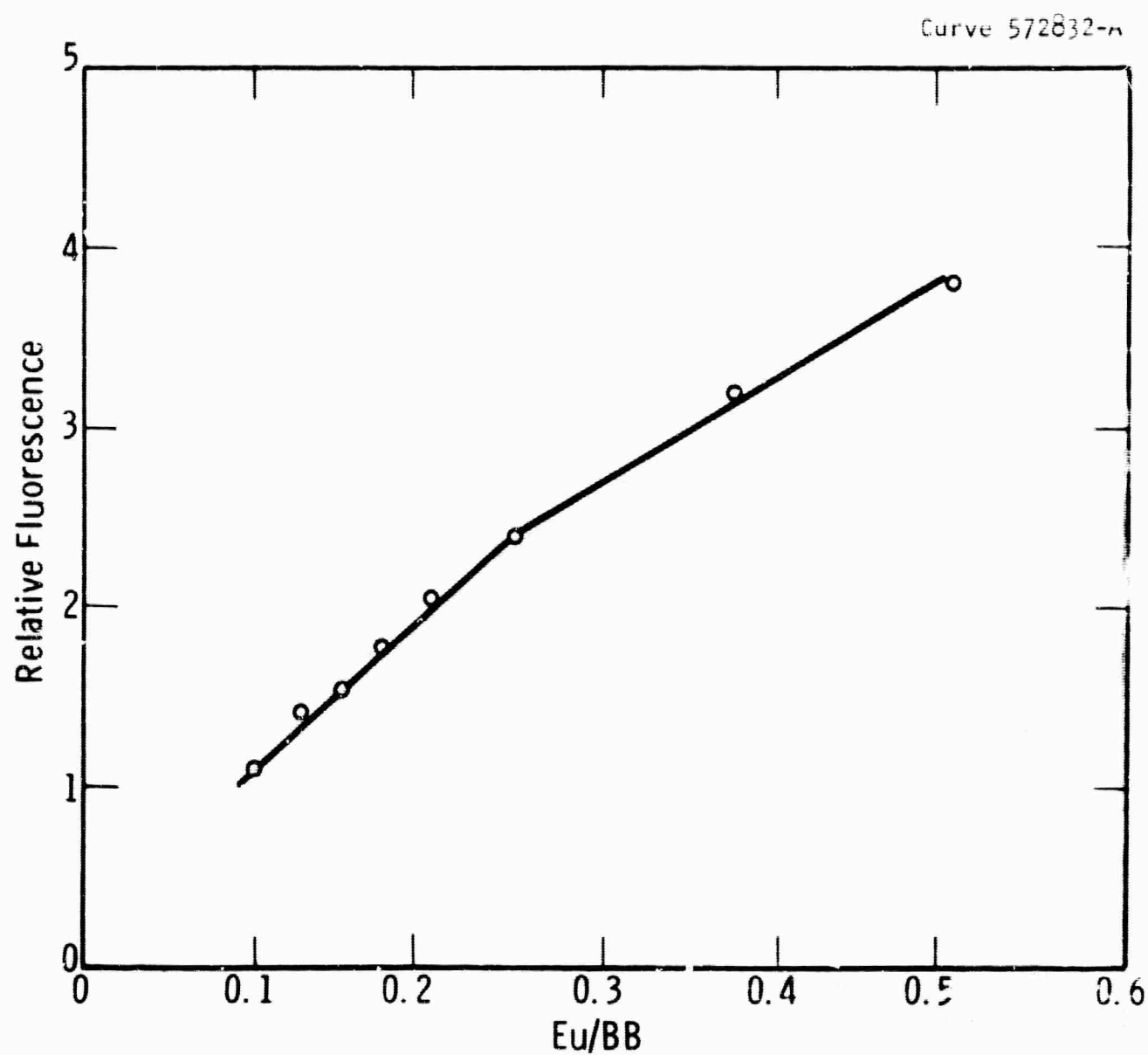


Fig. 12. Relative europium fluorescence of water solutions 0.04 M in Na p-Benzoylbenzoate and containing various quantities of NaEuEDTA.

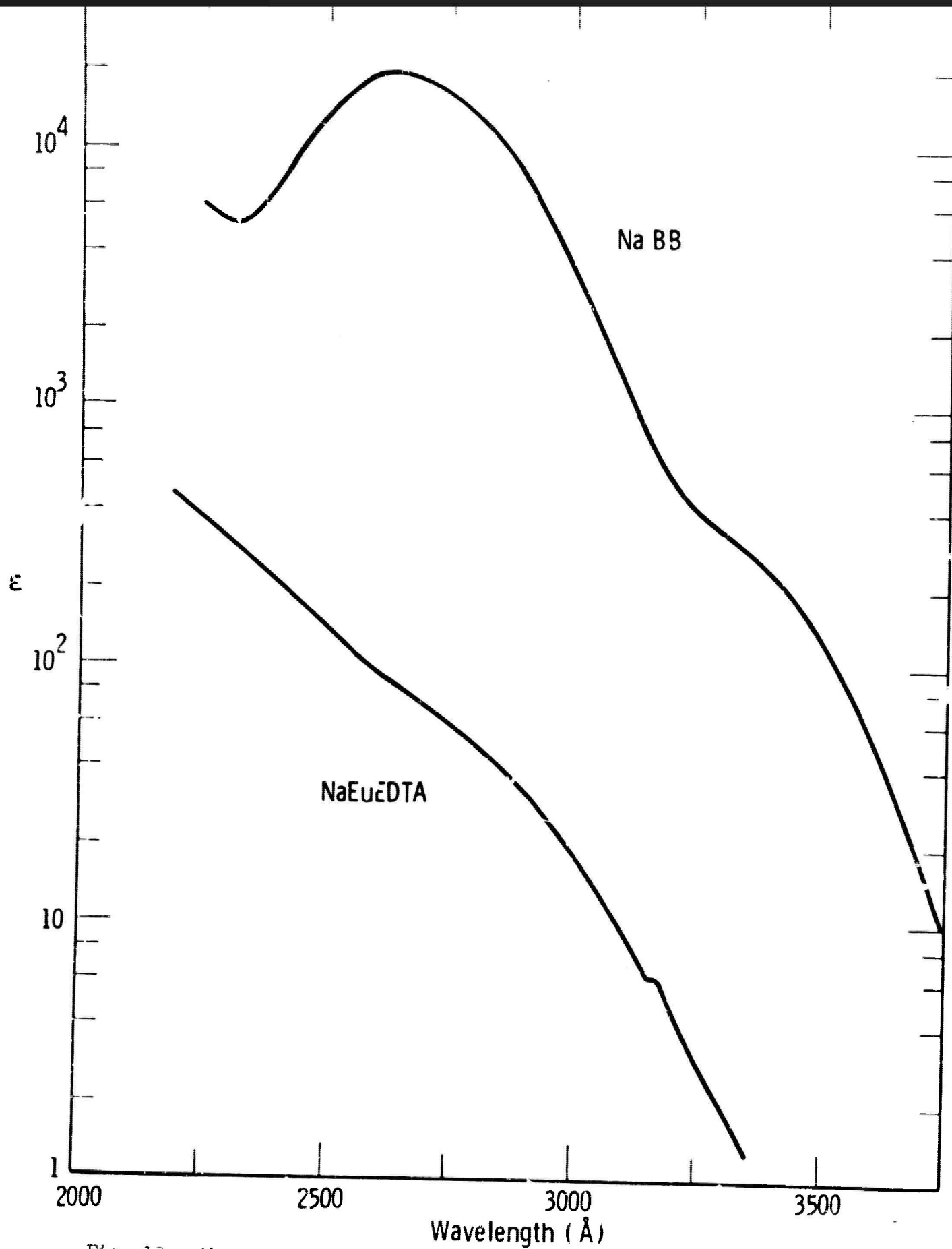


Fig. 13. Absorption spectra of sodium *p*-benzoylbenzoate and of sodium europium ethylenediaminetetraacetate in water.

comparable molar quantities, absorption is almost entirely due to the BB^- ions at all wavelengths. At the longer wavelengths, absorption involves the $n-\pi^*$ transition associated with the keto carbonyl group of the BB^- . The absorption band due to this transition appears as a shoulder on the long wavelength side of the more intense $\pi-\pi^*$ band which peaks at 263 m μ .

El-Sayed and Bhaumik⁽²⁾ have recently reported transfer of energy absorbed through the $n-\pi^*$ transition of benzophenone to the chelate europium hexafluoroacetylacetonate in an ether-pentane-ethanol mixture. It is not clear whether mixed ligand complex formation or intermolecular energy transfer is involved in this system. Direct bonding of benzophenone to europium would, of necessity, be through the lone pair electrons of the keto carbonyl group. In contrast to this, attachment of the BB^- ion studied here is almost certainly through the carboxylate group. (Complexes between carboxylate anions and the rare earths in aqueous solution are well known.)

Solutions Containing o- or m-benzoylbenzoate

It was of interest to study the fluorescence properties of analogous systems containing $EuEDTA^-$ and the o-benzoylbenzoate (o- BB^-) or m-benzoylbenzoate (m- BB^-) ions where the COO group is attached to the o and m positions respectively in the top left hand drawing in Fig. 2. Solutions in H_2O which were 0.01M in $EuEDTA^-$ and 0.2M in o- BL^- or m- BB^- had fluorescence efficiencies lower by a factor of at least 50 compared to the same system containing the p-benzoylbenzoate anion. These low efficiencies could be due either to a lower tendency

for o-BB⁻ or m-BB⁻ to form mixed ligand complexes with EuEDTA⁻ or to low intramolecular transfer efficiency of energy within the mixed complexes. The tendency to form mixed complexes with o-BB⁻ or m-BB⁻ was not further investigated. Simple salt formation readily takes place, however, between Eu³⁺ and o-BB⁻ or m-BB⁻ as shown by the isolation of the hydrated compounds Eu(o-BB)₃ and Eu(m-BB)₃. Both of these solid compounds show significant fluorescence characteristic of Eu³⁺, with however, lower fluorescence than the solid salt derived from the para isomer.

3.2 Europium Fluorenone Carboxylate Complexes

Results obtained with the benzoylbenzoates (Section 3.1) suggested that europium salts or complexes derived from the four possible fluorenone monocarboxylic acids (top right hand drawing in Fig. 2) might also have suitable optical absorption properties for efficient utilization of pump light. The results of studies outlined below however indicate that intramolecular energy transfer does not occur in these compounds to Eu³⁺ or Tb³⁺ although transfer does take place to Nd³⁺. Figures 14, 15 and 16 show that the fluorenone 1-, 2-, and 4-carboxylate anions (derived from the acids of Fig. 2 through the loss of the carboxylic hydrogen) do indeed have broad n-π* absorption bands in the region 350-450 mμ, of the proper intensity for efficient use of pump light. (The corresponding 3-isomer was not studied since, in our hands, published preparative procedures did not give significant yields of product.)

Solutions prepared in water or heavy water containing europium ethylenediaminetetraacetate and the fluorenone 1-, 2-, or

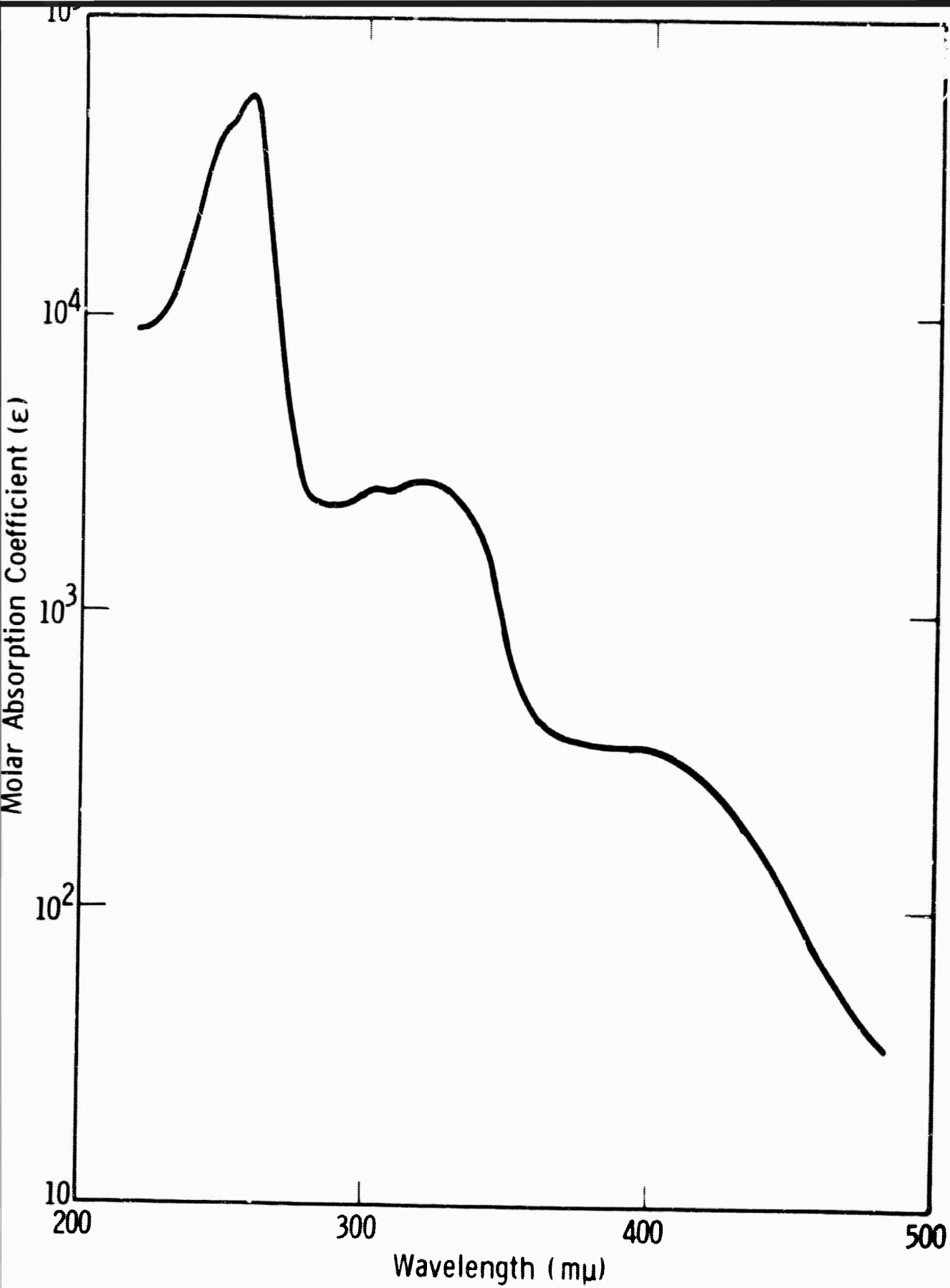


Fig. 14. Absorption spectrum of fluorenone-1-carboxylic acid in 0.1 M aqueous NaOH.

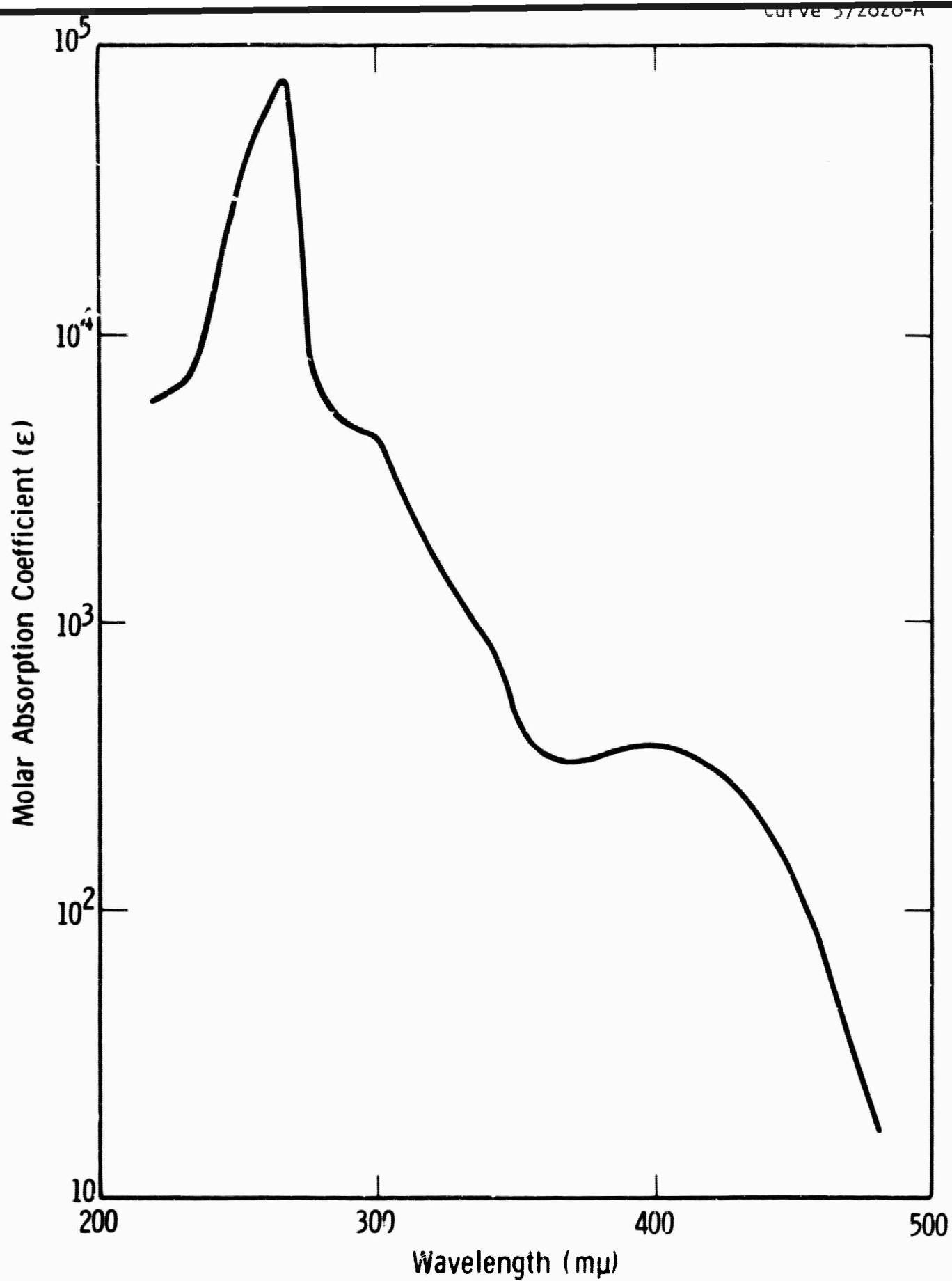


Fig. 15. Absorption spectrum of fluorenone-2-carboxylic acid in 0.1 M aqueous NaOH.

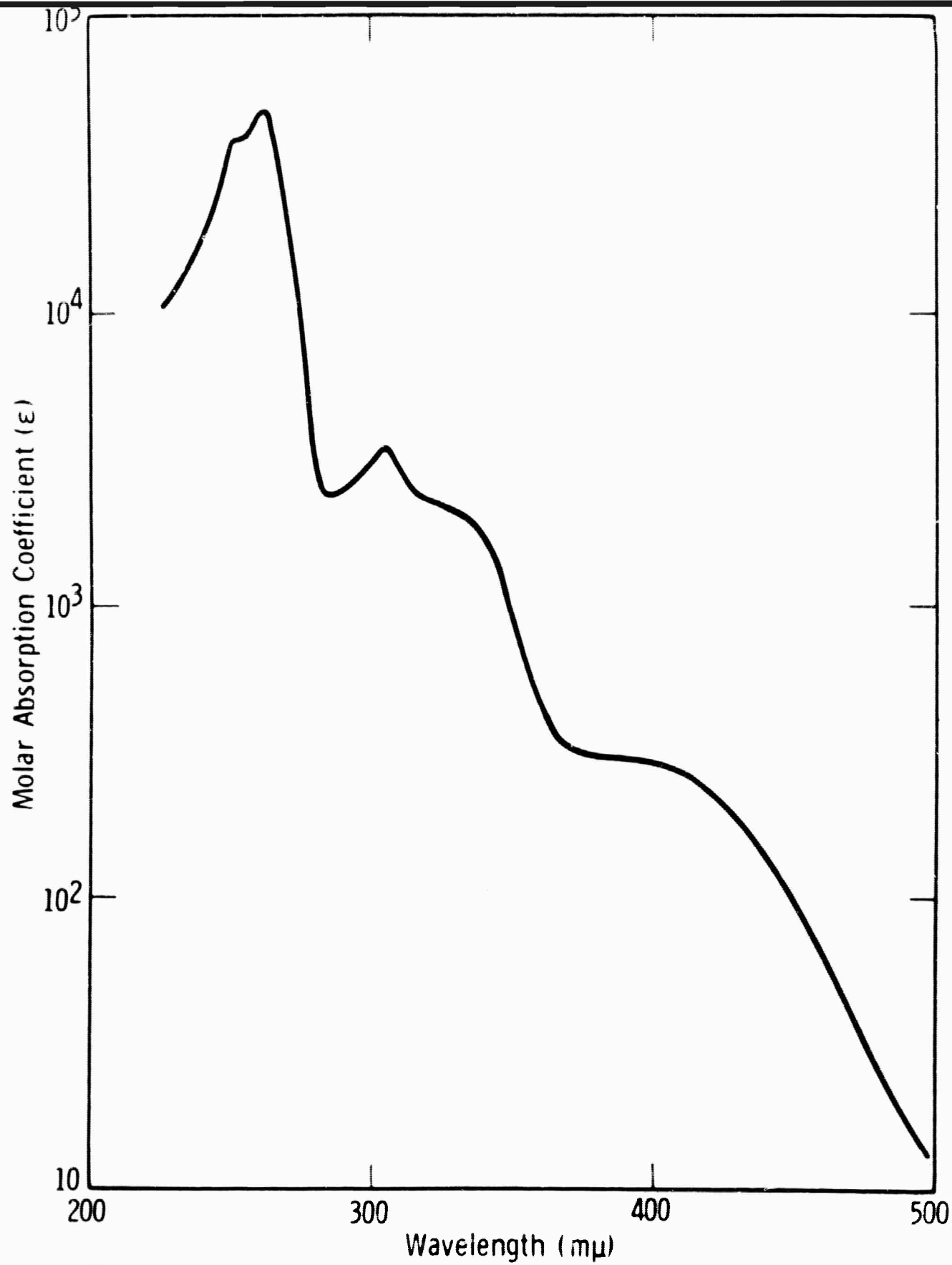


Fig. 16. Absorption spectrum of fluorenone-4-carboxylic acid in 0.1 M aqueous NaOH.

4-carboxylate anion did not give visible fluorescence when irradiated with ultraviolet light. These negative results could be due to lack of complex formation between the fluorenone carboxylate anion and EuEDTA^- or to inefficient energy transfer between bonded fluorenone-carboxylate and europium. To obtain further information on this point we have isolated solid (hydrated) salts of the composition $(\text{C}_{14}\text{H}_8\text{O}_3)_3 \text{Ln}$, where Ln is Eu, Tb or Nd. None of the Eu and Tb salts show visible fluorescence at room temperature, apparently due to poor intramolecular energy transfer of absorbed energy.

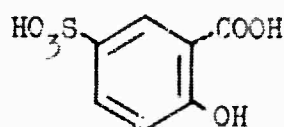
The Nd salt derived from fluorenone 2-carboxylic acid, however, shows with ultraviolet excitation between 3300 Å and 4300 Å the characteristic emission spectrum of Nd^{3+} . The absence of Nd^{+3} absorption⁽²¹⁾ in the range 3800 to 4300 Å and the observed Nd^{+3} fluorescence indicate that intramolecular energy transfer does take place to the metastable $^4\text{F}_{3/2}$ level of Nd^{+3} . Evidently the metastable level of Nd^{+3} is low enough for transfer to take place while the metastable $^5\text{D}_4$ and $^5\text{D}_0$ levels of Tb^{+3} and Eu^{+3} , respectively lie too high for effective transfer to take place in this compound.

3.3 Mixed Ligand Complex Formation Between Terbium Ethylenediaminetetraacetate and the 5-sulfosalicylate Ion

In addition to the work described above for europium we have also considered the use of trivalent terbium in mixed ligand complex systems in aqueous solution. This work was carried out in an effort to obtain a Tb^{+3} chelate system soluble in heavy water with an improved absorption band over those systems discussed in

Section 2.4. This effort was successful and a system having a very high quantum efficiency in D_2O at room temperature was obtained.

We have found that bright green fluorescence, characteristic of the Tb^{+3} ion, is obtained from H_2O and D_2O solutions containing mixtures of Tb^{+3} , the trivalent anion of 5-sulfosalicylic acid, (SSA^{-3}) and the ethylenediaminetetraacetate ion ($EDTA^{-4}$). The structural formula of 5-sulfosalicylic acid is shown below.



Maximum fluorescence intensity requires the presence of both SSA^{-3} and $EDTA^{-4}$. Measurements of fluorescence and optical absorption as the relative quantities of the reactants Tb^{+3} , SSA^{-3} , and $EDTA^{-4}$ are varied indicating that definite mixed ligand complexes exist in solution. For a solution prepared from equal molar quantities of the three reactants the principal fluorescent species appears to be the ion $[Tb(SSA)(EDTA)]^{-4}$.

Figure 17 gives the room temperature fluorescence spectrum of a D_2O solution 0.02M in each of three reactants. The spectrum arises from transitions within the $4f^{(22)}$ shell of Tb^{+3} . Comparison of Fig. 17 with the spectrum of Tb^{+3} in $LaCl_3^{(22)}$ indicates that the four emission groups in Fig. 17 represent transitions from the 5D_4 level to the 7F_6 , 7F_5 , 7F_4 , and 7F_3 levels at 480-510, 530-565, 575-605, and 610-640 mμ, respectively.

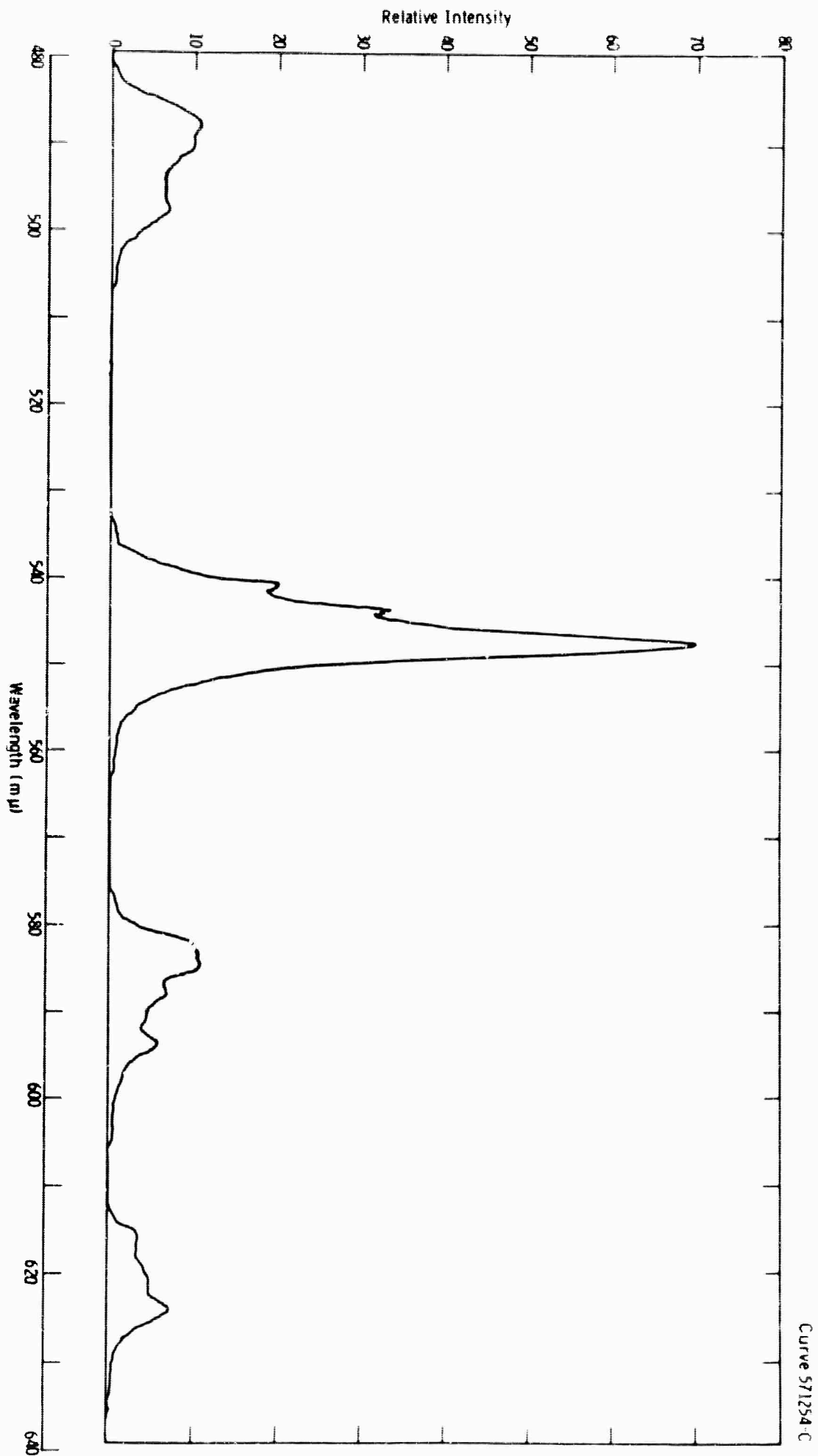


Fig. 17. -Fluorescence spectrum of 0.02M [TMSSA(EDTA)]⁻⁴ in D₂O at 300°K with near UV excitation and 4 Å resolution

The decay of the Tb^{+3} fluorescence in this solution, at both room temperature and $5^{\circ}C$, is exponential with a decay time of 2.4 milliseconds. The absolute quantum efficiency of the solution (excited with 2537 Å radiation) is 0.9 ± 0.1 , and this value is insensitive to temperature over the range 5 to $25^{\circ}C$.

Absorption of ultraviolet radiation by the solutions is primarily through the SSA^{-3} ions. Figure 18 shows the absorption spectra of SSA^{-3} (in 0.1M NaOH to suppress hydrolysis) and of NaTbEDTA in water. The absorption by SSA^{-3} is much greater at all wavelengths. Absorption spectra of Na_3SSA -NaTbEDTA mixtures are similar to the spectrum of SSA^{-3} alone, with some changes in position and intensity of absorption maxima due to complex formation and to hydrolysis.

The discrete line emission, the high quantum efficiency and favorable decay time all suggest the present system as a likely candidate to display laser action. In tests to date, however, no evidence for stimulated emission has been obtained. Possibly, this may be associated with the choice of rare earth ion since laser action has not yet been demonstrated in other systems containing terbium. It was also observed that some photodecomposition occurs in the present system under intense ultraviolet illumination.

In summarizing the work in Section 3 on chelate systems in heavy water, it is apparent that photodecomposition of the chelates emerges as a major problem. There is no reason to believe however that this problem cannot be overcome when more fundamental information is obtained on rare earth water soluble systems in general and the

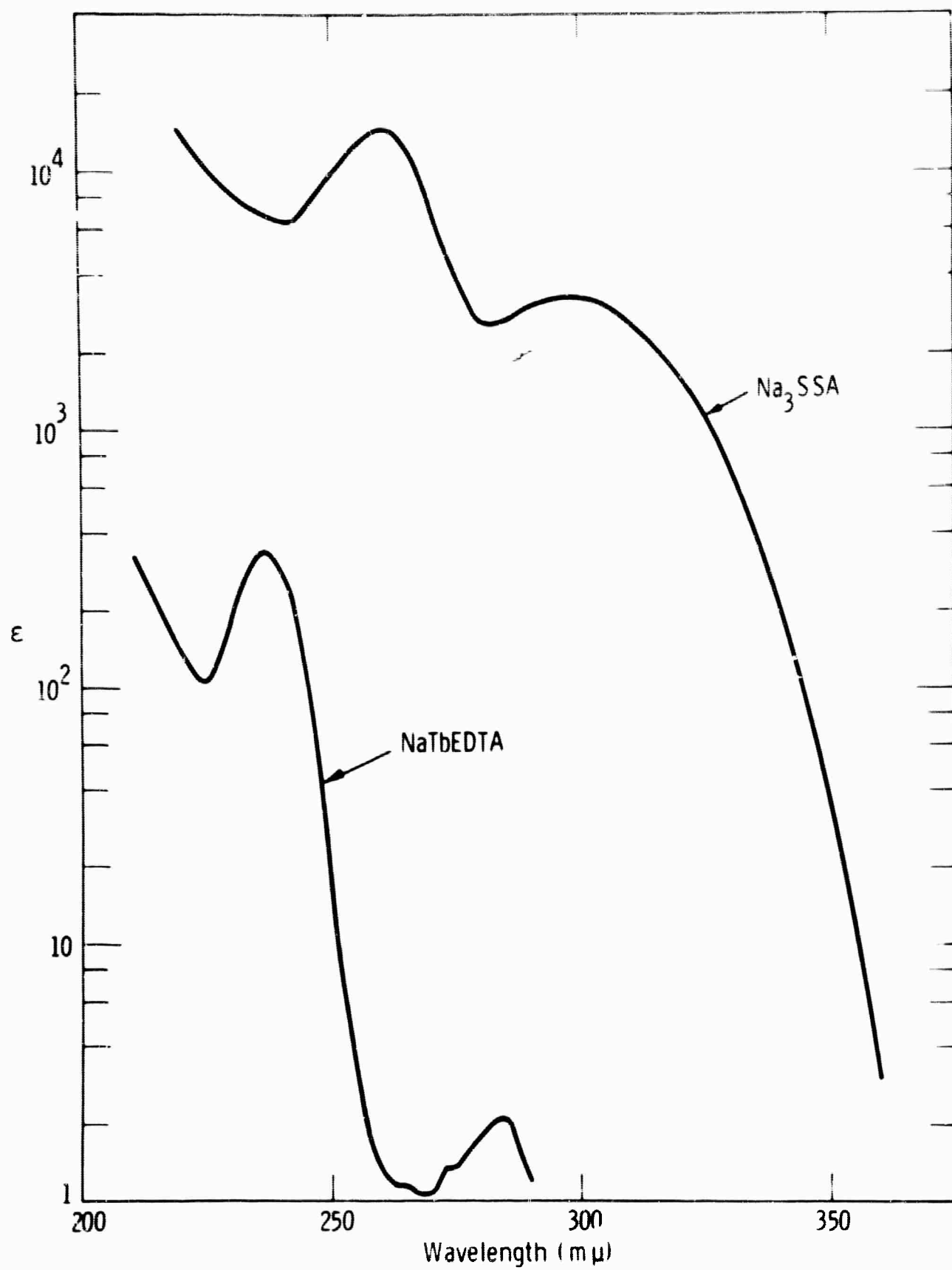


Fig. 18.—Absorption spectra of Na_3SSA and NaTbEDTA in H_2O

photodecomposition mechanisms of such systems in particular. The importance of this work is clearly apparent since the feasibility of obtaining both Tb^{+3} and Eu^{+3} chelate systems with high quantum efficiency and comparatively favorable absorption bands in heavy water solutions at room temperature has been demonstrated.

4. Chelates Soluble in Organic Solvents

Recently, room temperature operation of a liquid laser was reported by Samelson, Iempicki, Brecher and Brophy.⁽²³⁾ The material which they used was a solution in acetonitrile of the piperidinium salt of the tetrakis form of europium benzoyltrifluoroacetate.

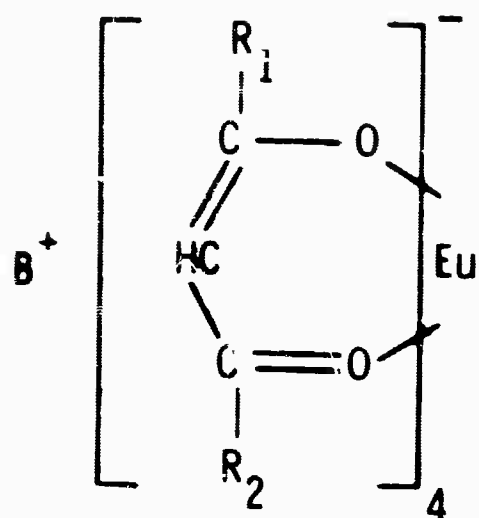
This salt is the tetrakis β -diketone chelate I shown in Fig. 19 where $R_1 = CF_3$, $R_2 = \text{phenyl}$ and $B = \text{piperidinium}$. Although the chelates I and II in Fig. 19 are usually soluble only in organic solvents, the work with these materials was undertaken in the hope of obtaining information which would aid in designing chelates for use in heavy water solutions.

4.1 Salts Derived from Europium Benzoyltrifluoroacetate

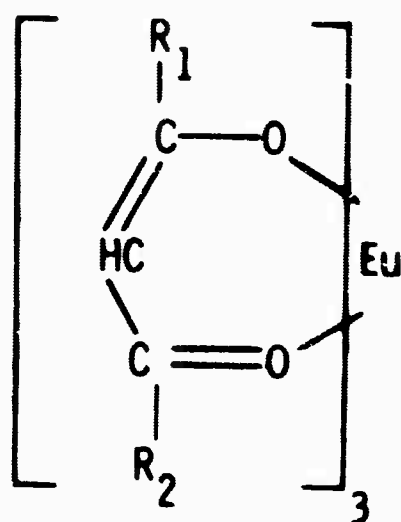
In order to study the effect on laser performance of varying B in I shown in Table II, we have prepared and studied a number of such salts of europium benzoyltrifluoroacetate (EuBTA). We have found that laser performance is not independent of B .

Subsequent to the success of Samelson, et al⁽²³⁾ but prior to December 31, 1964, we also succeeded in obtaining laser action in the piperidinium salt in acetonitrile. In addition, we succeeded in obtaining laser action in the diethylamino salt in acetonitrile. The latter material is a new one not previously reported to give laser oscillations. Subsequent to December 31, laser action has been successfully achieved for the first

Dwg. 745A543



I
Tetrakis



II
Tris

Fig. 19. Europium chelates derived from β -diketones.

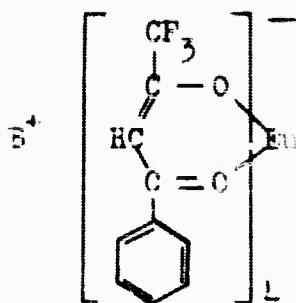
time in eight more of the salts in acetonitrile. We have not, however, been able to achieve laser action in all of the salts tested indicating that the cation does have an effect on laser threshold. The mechanism of this effect is not yet understood. A detailed spectroscopic investigation is in progress. The laser threshold results at room temperature, 0°C and -30°C are shown in Table II. The laser cell and other apparatus used in measuring these thresholds are described in Section 4.2.

The europium chelates I are obtained, in general, by the reaction of EuCl_3 or $\text{Eu}(\text{NO}_3)_3$, in a water-ethanol solution, with the β -diketone and the organic base both present in excess. The tetrakis chelate was not obtained, however, by the reaction of EuCl_3 with benzoyltrifluoroacetone and triethanolamine. Instead, the hydrated tris chelate II, shown in Fig. 19 where $\text{R}_1 = \text{CF}_3$, $\text{R}_2 = \text{phenyl}$ resulted. The tris chelate has been included, for comparison, in the studies described below.

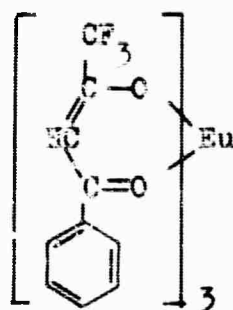
So far, laser action near room temperature has been obtained only with some of the tetrakis forms (I in Table II) of EuBTA but not with the tris form (II in Table II). The reason for this is clear since the relative fluorescent intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the tris form is about a factor of ten lower than that of the tetrakis form as shown in Figs. 20 and 21. The reason for the higher quantum efficiency of the tetrakis form over the tris form is not yet completely clear. It seems reasonable to expect, however, that the extra ligand around the europium ion in the tetrakis form aids in protecting the europium ion from the solvent to the extent that less energy is dissipated non-radiatively to the solvent molecules. The absorption spectra of these materials are shown in Figs. 22 and 23. If the molar absorption coefficient ϵ is 5×10^4 and the concentration is 10^{-2} M, the penetration depth for light is about 10^{-2} mm. Therefore, effective pumping to depths of 0.5 mm or more must occur in a comparatively narrow wavelength range on the long wavelength wing of the absorption band. This raises the threshold.

Table II*

Measured Threshold Energy for Various β -diketone
Chelates of Structure:



I
Tetrakis



II
Tris

Threshold Energy in Joules
(Concentration: 5×10^{-2} M in acetonitrile)

B	Formula	24°C	0°C	-30°C
piperidinium	I	660	200	No Test
tetrabutyl ammonium	I	>1800	>1800	>1800
diethylamino	I	No Test	800	No Test
triethylamino	I	No Test	1100	No Test
n-butylamino	I	>1500	800	No Test
pyridinium	I	No Test	800	No Test
isoquinolinium	I	>1200	1400	No Test
ethanolamino	I	>1200	1300	No Test
tetramethyl guanidinium	I	>1200	800	No Test
tetramethylammonium	I	>1200	700	No Test
---	II	>1800	>1800	>1800
benzylamino	I	>1200	900	No Test

*The symbol > signifies that laser action was not observed up to the indicated energy and that tests at higher energies at that temperature were not conducted.

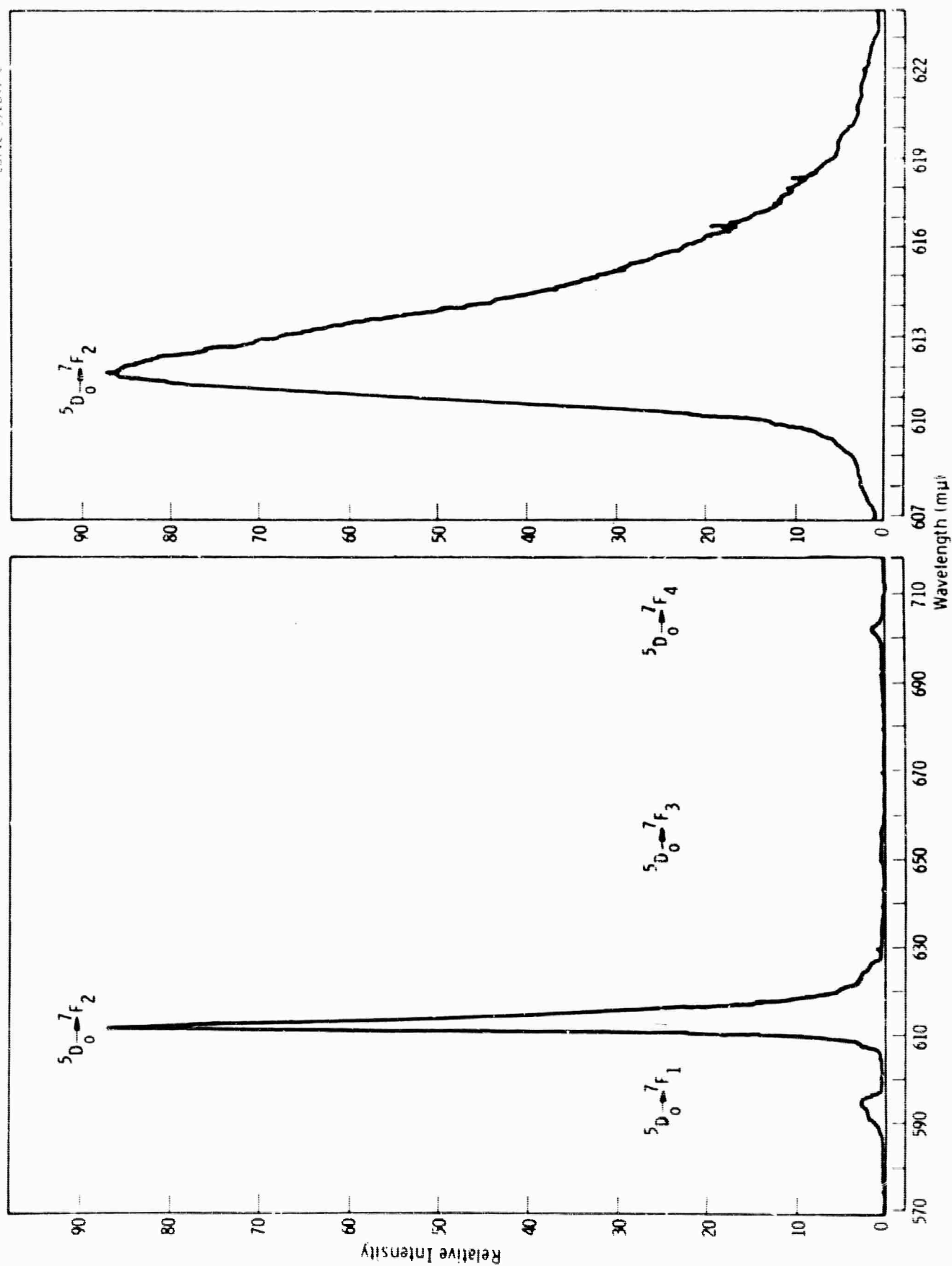


Fig. 20. Fluorescence spectrum of piperidinium europium tetrakis benzoyltrifluoroacetate, 0.05 M in acetonitrile at room temperature (2Å resolution, near ultraviolet excitation).

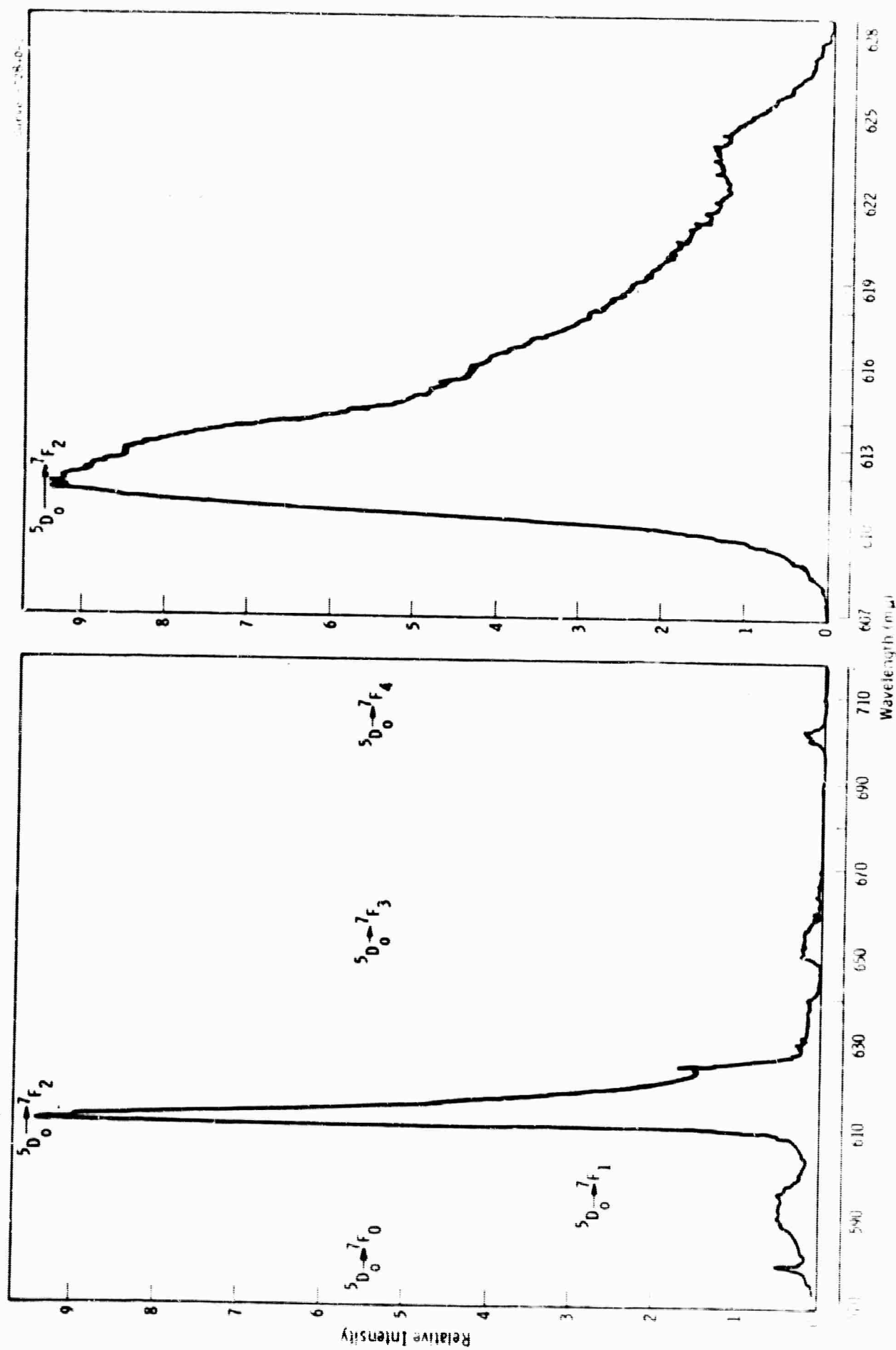


FIG. 21. Fluorescence spectrum of europium tris(phenyltrifluoroacetate), 0.55 M in acetonitrile at room temperature, (2Å resolution, near ultraviolet excitation).

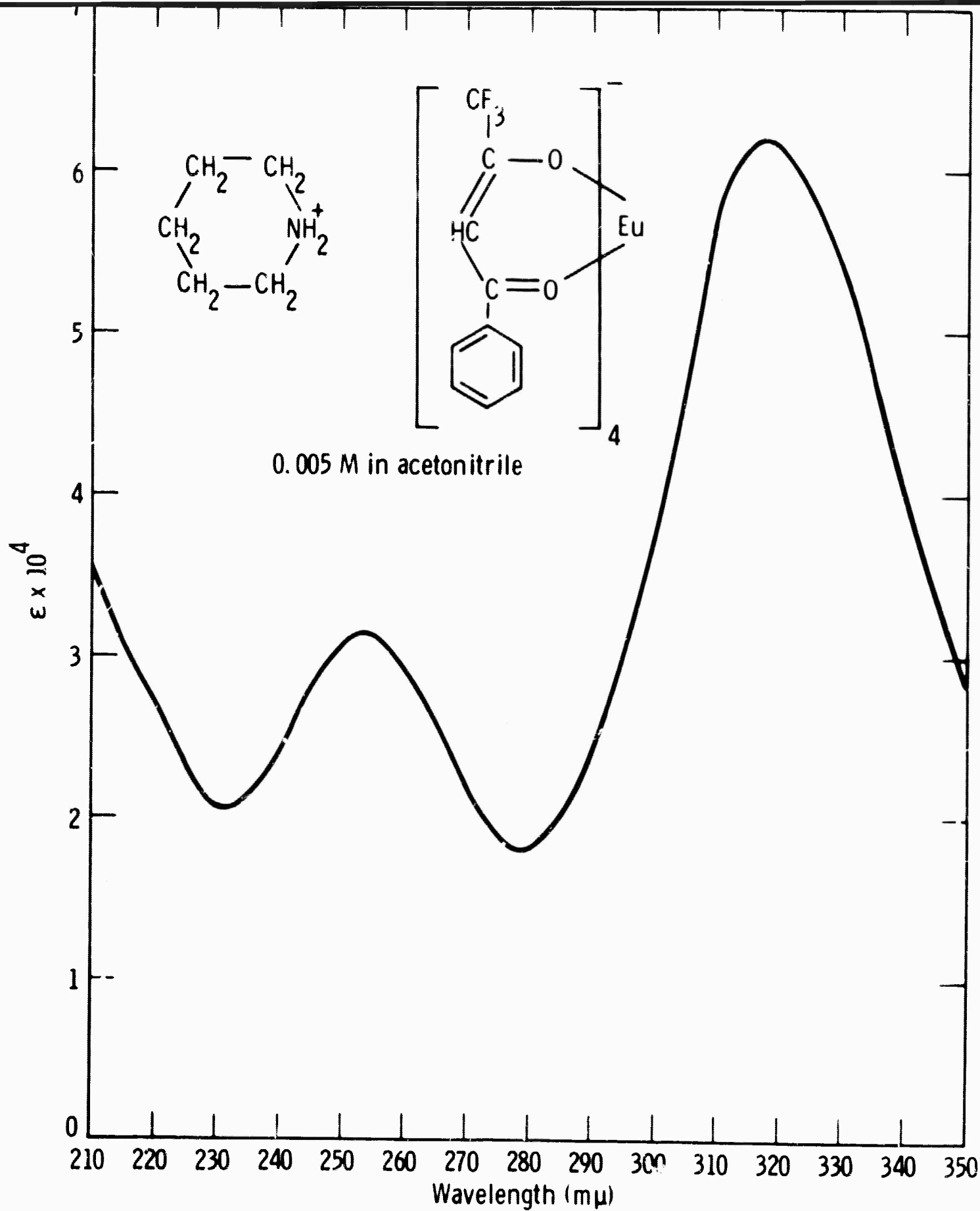


Fig. 22. Ultraviolet absorption spectrum of piperidinium europium tetrakis benzoyltrifluoroacetate

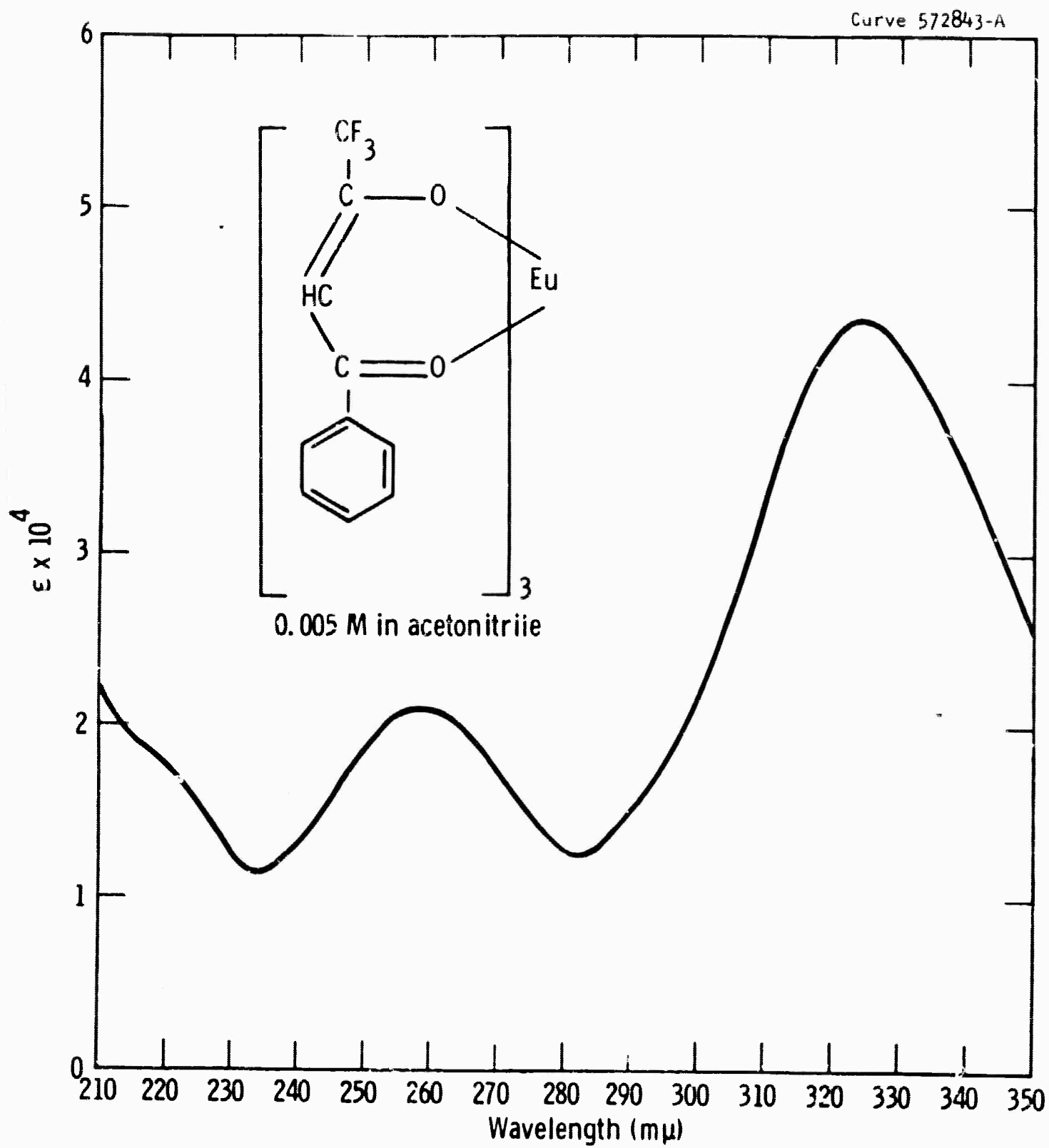


Fig. 23. Ultraviolet absorption spectrum of europium tris benzoyltrifluoroacetate

4.2 Laser Experiments Near Room Temperature

4.2.1 Apparatus

The laser cell used in all experiments unless otherwise noted was a 1 mm inside diameter quartz capillary tube with an active pump length of 6.7 centimeters and a mirror spacing of 9.3 centimeters. The ends of the tube were first polished flat to $1/10\lambda$ and parallel to about ten seconds of arc. Quartz disks flat to $1/10\lambda$ and parallel to about two seconds of arc were wrung on to the ends of the tube. Each disk was then epoxied to the tube. Multilayer films having better than 99 percent reflectivity at 6120 Å were deposited on the outside surface of each disk and are, therefore, not in contact with the liquid material within the capillary. Three EG and G flash lamps (FX-42) are placed at 120° intervals around the cell with Corning CS-7-59 filters inserted between the lamps and the cell. A heavy aluminum foil is then wrapped around the outside of the three lamps. The cell assembly is held in an insulated chamber so that the temperature may be both changed and stabilized.

The output from one end of the cell is allowed to fall on the entrance slit of a 1/2 meter Jarrell Ash monochromator. A partially transparent mirror placed two inches beyond the exit slit splits the output beam—one part going to a photomultiplier and the remainder to a lens. The lens magnifies the spectrum at the exit plane ten times. The magnified image is recorded on film. In this way, a photomultiplier recording can be obtained of the laser output pulse and at the same time spectral narrowing demonstrated by the width of the image formed by the lens on the film. For example, if the entrance slit of the monochromator

is a 100 microns and monochromatic radiation falls on the entrance slit, the image formed on the film will be about one millimeter wide. If, on the other hand, a band thirty-two Angstroms wide falls on the entrance slit opened to 100 microns, the image on the film will be about one centimeter wide since the dispersion at the exit slit plane is 32 Å per millimeter. Therefore, spectral narrowing is easy to demonstrate by this technique down to about $1/2$ Å which is the resolution limit of the monochromator.

4.2.2 Laser Characteristics of the Piperidinium Salt of Europium Benzoyltrifluoroacetate

Figure 24 is a typical photomultiplier recording showing both the flash lamp trace and the output laser spikes. Figure 25 is a one-to-one reproduction of the film image taken at the same time Fig. 24 was recorded. Since the line is about one millimeter wide, the spectral width of the output beam is 3 Å or less. Since the width of the spontaneously emitted line (Fig. 20) is about 33 Å, spectral narrowing is clearly evident.

The output beam divergence has been measured. Figure 26 shows a photograph of the beam output at a distance of 77 inches from one end of the cell. (The structure, presumably due to the optical inhomogeneity of the liquid, is clearly evident). This beam divergence is near the aperture limit of the 9.3 centimeter cell. In order to obtain a true value for the beam divergence, a cell with a mirror separation of 6.0 centimeters and with an effective pump length of 3.6 centimeters was constructed. The threshold for laser action at 0°C with this cell is 1830 joules. The beam divergence measured with this cell near threshold was about 1.2×10^{-2} radians but was not aperture limited.

Since the diffraction limited beam angle for this cell is about 1.5×10^{-3} radians, the measured output beam divergence angle is larger by

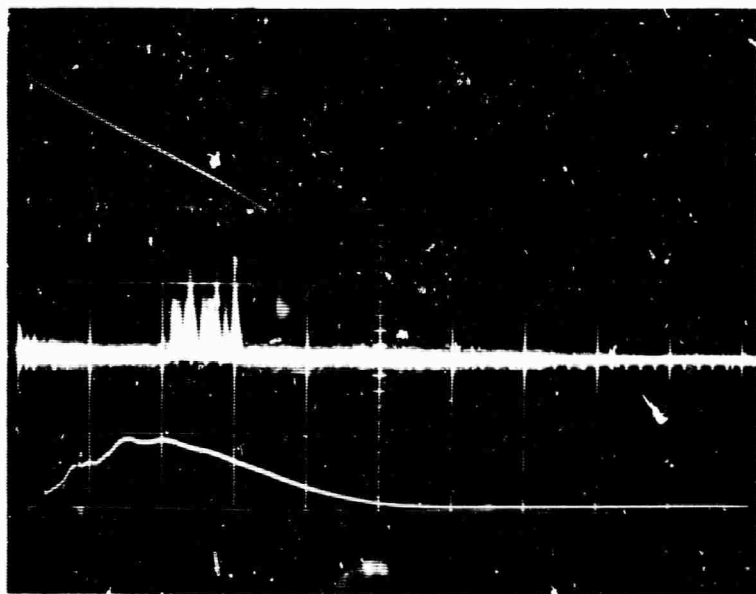


Fig. 24. Top: Photomultiplier recording of light output from $5 \times 10^{-2}M$ solution of the piperidinium salt of EuBTA in acetonitrile. Temperature: $0^{\circ}C$. Scale: 200 usec./cm from left to right. Bottom: Recording of flash lamp light. 1350 J input (2.25 times threshold).



Fig. 25. Taken at same time as Fig. 24. One to one reproduction of film image (see text) showing spectral width of spikes in Fig. 24 to be 3A or less.

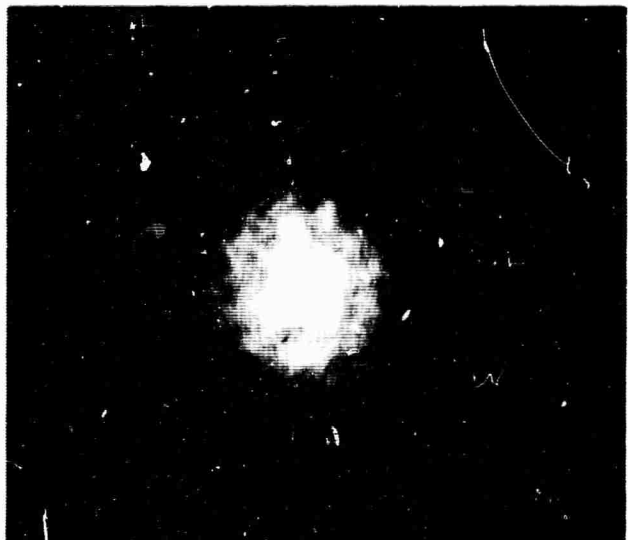


Fig. 26. Photograph of output beam at 77 inches from other end of cell. (Taken at same time as Fig. 24).

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about a factor of 8. The laser output radiance is inversely proportional to the square of the beam divergence angle. Therefore, for systems requiring high radiance, the comparatively large beam divergence represents an important problem.

The exact dependence of beam divergence angle on optical homogeneity of the laser material during laser action is not yet understood in detail. One would expect, however, that the refractive index gradients created in the material during the pumping process (see Sections 2.2 and 2.3) are important in causing the beam angle to be larger than the diffraction limit.

4.2.3 Laser Action in the Benzylamino Salt of Europium Benzoyltrifluoroacetate

The output spiking observed for the piperidinium salt is typical of that observed for the other salts which lase near room temperature. For example, Fig. 27 is a photomultiplier recording showing the output spiking in the benzylamine salt of EuBTA at a flash lamp energy about 1.04 times threshold. When the flash lamp energy is increased to about 1.2 times that necessary for threshold, the laser spikes become more pronounced compared to the signal due to spontaneous emission as shown in Fig. 28. The spectral width of the output spikes shown in Fig. 28 are 3 Å or less as shown in Fig. 29.

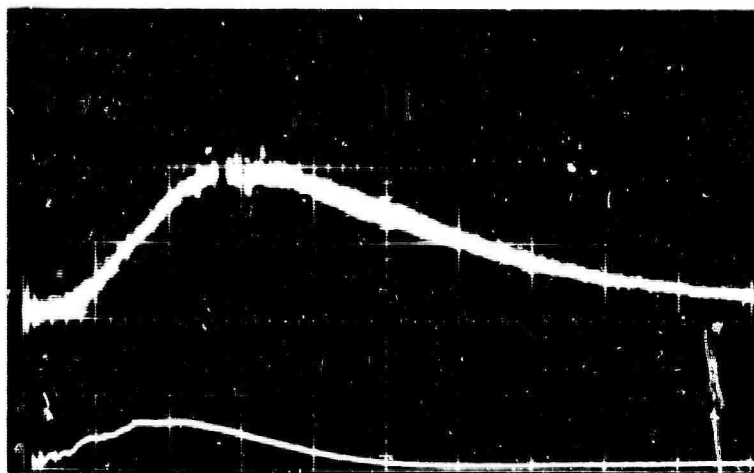


Fig. 27. Top: Photomultiplier recording of light output from 5×10^{-2} M solution of benzylamino salt of EuBTA in acetonitrile. Scale: 200 usec. from left to right. Temperature: 0°C . Bottom: Flash lamp light recording for 935 J input.

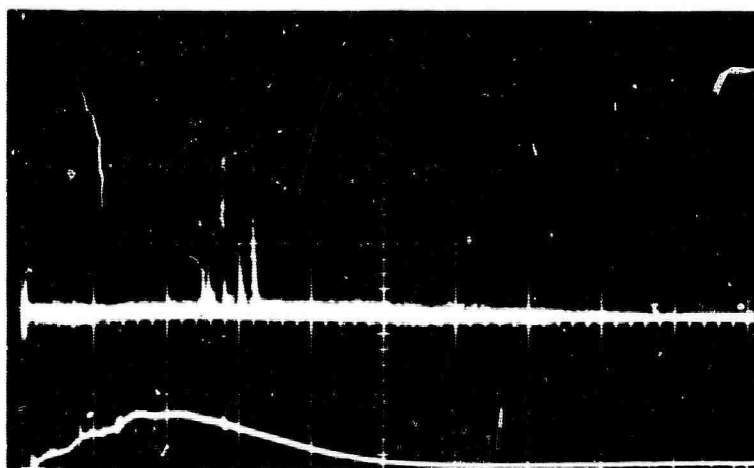


Fig. 28. Same as Fig. 27 except for 1100 J input to flash lamps.



Fig. 29. One to one reproduction of film image (see text) showing spectral width of spikes in Fig. 28 to be 3A or less.

5. Experimental Procedures

5.1 Materials

Ethylenediaminetetraacetate chelates

The salts $\text{NaEuEDTA} \cdot 8\text{H}_2\text{O}$ and $\text{NaTbEDTA} \cdot 6\text{H}_2\text{O}$ were prepared by reacting Eu_2O_3 or $\text{Tb}(\text{OH})_3$ with ethylenediaminetetraacetic acid and NaOH in water solution.²⁴ The products were purified by dissolving in water and reprecipitating with acetone. The purified salts were air-dried at room temperature.

Benzoylbenzoic acids

p-benzoylbenzoic acid was obtained from K and K Laboratories, Plainview, N. Y. The compound was recrystallized from ethanol. K and K Laboratories o-benzoylbenzoic acid was dissolved in dilute aqueous KOH and reprecipitated with HCl. The precipitated material was recrystallized from ethanol-water. m-benzoylbenzoic acid was synthesized by the method of White et al.⁽²⁵⁾ The product was purified by dissolving in toluene and precipitating with petroleum ether.

Solid Europium Benzoylbenzoates

The o-, m-, or p-benzoylbenzoic acid (0.01 mole) was stirred in a flask with a mixture of 100 ml water and 10 ml 1M NaOH until dissolved. An aqueous solution of Lindsay 99.9 percent EuCl_3 (7.43 ml of 0.444M) was added dropwise to the stirred solution over a period of 5 minutes. A white precipitate formed throughout the addition. After stirring for an additional 1/2 hour the solid was filtered off, washed with water and dried in vacuo at room temperature. The products from the m- and p-benzoic acids were recrystallized by

dissolving in warm methyl ethyl ketone. The solution was filtered warm through a glass pressure filter and 3 volumes of water were added to the cooled solution. The mixture was allowed to stand overnight in the refrigerator. The solid was filtered off and dried in vacuo at room temperature. Compositions of the products are given in Table III. The analytical figures for the o-compound indicate that some hydrolysis has occurred. Analyses were not improved by recrystallizing this compound.

Table III

Composition of Solid Europium Benzoylbenzoates

Compound	Yield %	%C	%H	%Eu	%H ₂ O ^c
(o-C ₁₄ H ₉ O ₃)Eu·4H ₂ O	89 ^a	calcd. 56.1	3.96	17.8	8.0
		found 54.8	3.96	17.8	8.5
(m-C ₁₄ H ₉ O ₃)Eu·2H ₂ O	85 ^b	calcd. 58.4	3.63	17.6	4.2
		found 58.1	3.72	18.0	4.0
(p-C ₁₄ H ₉ O ₃)Eu·2H ₂ O	95 ^b	calcd. 58.4	3.63	17.6	4.2
		found 58.4	3.74	17.4	4.0

^aNot recrystallized.

^bRecrystallized.

^cWeight loss on thermobalance to 150°C

Fluorenone carboxylic acids

Fluorenone 1-carboxylic acid was prepared by oxidizing fluoranthene according to the method of Fieser and Seligman.⁽²⁶⁾ Fluorenone 2-carboxylic acid and fluorenone 4-carboxylic acid were obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin. All three acids were recrystallized from glacial acetic acid. Attempts to prepare fluorenone 3-carboxylic acid by published methods were unsuccessful.

Solid rare earth fluorenone carboxylates

One hundred ml water containing 10 ml of 1M standard aqueous NaOH was stirred with an excess of the fluorenone carboxylic acid until no more would dissolve. The excess solid was removed by filtration. To the filtrate was added dropwise from a burette the calculated volume of standardized 0.5 M aqueous rare earth chloride. The reaction mixture was allowed to stand several hours at room temperature. The solid (frequently gelatinous) was then filtered off, washed with water, and dried in vacuo at room temperature. Compositions of products are given in Table IV.

Table IV
Composition of Solid Rare Earth Salts of
Fluorenone Carboxylic Acids

Compound	Yield %	%C	%H	%Metal
$(2-C_{14}H_7O_3)_3Na \cdot 3H_2O$	96	calcd. 58.1	3.14	16.6
		found 57.8	2.70	16.4
$(1-C_{14}H_7O_3)_3Eu \cdot 2H_2O$	93	calcd. 58.8	2.94	17.7
		found 58.0	2.97	18.0
$(2-C_{14}H_7O_3)Eu \cdot 4H_2O$	92	calcd. 56.5	3.27	17.0
		found 56.7	2.99	17.8
$(4C_{14}H_7O_3)Eu \cdot 2H_2O$	92	calcd. 58.8	2.94	17.7
		found 59.0	2.76	18.6
$(2-C_{14}H_7O_3)Tb \cdot 3H_2O$	96	calcd. 57.2	3.08	18.0
		found 56.3	2.62	18.3

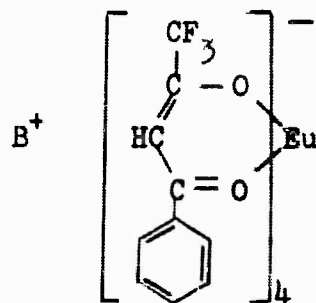
β -Diketone chelates

Tetrakis chelates of the type T were prepared in a manner similar to that described by Melby et al. ⁽²⁷⁾ Compositions are given in Table V. Europium tris benzoyltrifluoroacetate dihydrate (II, $R_1 = CF_3$, $R_2 =$ phenyl) was prepared in the following manner: Benzoyltrifluoroacetone (3.89 g., 0.018 moles) and triethanolamine (2.68 g., 0.018 moles) were dissolved together in 60 ml warm 95 percent ethanol. $EuCl_3$ (0.004 moles as the calculated volume of a standardized 0.5 M solution) was dissolved in 20 ml water and added to the mixture. The combined mixture

was filtered and 80 ml water was added. After standing several days, the initially formed oil solidified. The solid was filtered off and air-dried at room temperature. Calcd. for $(C_{10}H_6O_2F_3)_3Eu \cdot 2H_2O$: C, 43.2; H, 2.66; N, 0%. Found: C, 43.3; H, 2.74; N, 0.02%.

Table V

Analysis of β -Diketone Chelates of Structure



B	% C	% H	% N	% F
piperidinium	calcd. 49.2	3.30	1.28	20.8
	found 49.4	3.33	1.34	20.9
tetrabutyl ammonium	calcd. 53.6	4.80	1.20	18.2
	found 54.2	5.16	1.27	17.8
diethylamino	calcd. 48.6	3.34	1.29	21.0
	found 49.0	3.54	1.44	19.9
triethylamino	calcd. 49.6	3.62	1.26	
	found 49.1	4.60	1.22	
n-butylamino	calcd. 48.6	3.35	1.29	
	found 48.0	4.01	1.24	
pyridinium	calcd. 49.5	2.77		
	found 49.6	2.97		

Table V (continued)

<u>B</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
isoquinolinium	calcd. 51.5	2.83		
	found 51.6	2.91		
ethanolamino	calcd. 46.9	3.01		
	found 46.5	3.14		
quinolinium	calcd. 41.5	2.83	1.23	
	found 52.2	2.96	1.28	
tetramethyl guanidinium	calcd. 47.9	3.40	3.72	
	found 48.0	3.58	3.73	

5.2 Spectroscopy

The fluorescence spectra were obtained with a 1 meter Jarrell Ash spectrometer having a dispersion at the exit plane of 16\AA per millimeter. An E.M.I. photomultiplier with an S-20 characteristic response was used to detect the signal at the exit plane. Except for Figs. 5,⁸ and 11, no correction was made for sensitivity change with recorded wavelength. The sensitivity at 7000\AA is less than that at 6000\AA by a factor of 2.1.

Absorption spectra were measured on a Cary spectrophotometer. Matched quartz sample cells were used having effective path lengths ranging from a few millimeters to 0.05 millimeters depending on the absorption coefficient of the material being measured.

6. Summary

Heavy water is a very attractive liquid laser solvent from the standpoint of high-radiance liquid laser development. This is because the small change in refractive index with respect to temperature near 6°C makes possible operation near the diffraction limit even under conditions of nonuniform heating occurring during pumping. In addition, heavy water is one of the most transparent condensed materials known near the expected output wavelength of 6120 Å. This fact, coupled with its good optical homogeneity, means that the loss per unit length near the output frequency will be small. This makes long lengths of active materials practicable. Finally, the low viscosity of heavy water at the proposed operating temperature (near 6°C), makes circulation of active material possible. A more detailed discussion of these points may be found in Section 2.

Because heavy water is the only solvent known at the present time which combines all of the features mentioned above, liquid laser research at the Westinghouse Research Laboratories has been and is aimed at developing heavy water soluble rare earth chelates. So far, both terbium and europium chelates have been synthesized which show typical rare earth ion fluorescence with high quantum efficiency in heavy water at room temperature. Part of this work which is described in Section 3 was done under the present contract. In addition, progress has been

made toward solving the general chelate absorption band problem by incorporating $n-\pi^*$ transitions which have characteristically lower intensity than the usual $\pi-\pi^*$ chelate absorption transitions. Part of this work was also done on the present contract and is included in Section 3. Unfortunately, the chelates studied to date which have high quantum efficiency in heavy water do not lase primarily because of photodecomposition during the pump process. There is no reason to believe, however, that this problem cannot be overcome although more work of a fundamental nature is needed in order to determine the structural chelate parameters important for good resistance to photodecomposition.

Laser action has been observed in 10 different salts of europium benzoyltrifluoroacetate (EuBTA) near room temperature in acetonitrile. As noted in Section 4, part of this work was also performed under the present contract. Other salts of EuBTA, however, do not lase, indicating that the ^{cation} ~~anion~~ is important in determining the laser capabilities of these materials. The beam divergence has been measured near threshold and found to be more than a factor of seven larger than the diffraction limit. This departure from the diffraction limit is evidently due primarily to refractive index gradients arising from thermal gradients set up in the material during flash excitation. Since the radiance is inversely proportional to the square of the beam divergence angle, a factor of seven departure from the diffraction limit represents an important effect. The potential increase in radiance gained by using heavy water as a solvent is therefore large.

It may be possible to modify the benzoyltrifluoroacetate chelate in such a way as to obtain water solubility. Studies along these lines as well as other water soluble chelate work is in progress.

7. Major Conclusions and Suggestions for Future Work

At the present stage of liquid laser research, the most important conclusions seem to be the following:

1. Heavy water should be a superior liquid laser solvent from the standpoint of its excellent optical homogeneity during optical pumping. Good optical homogeneity is required if the radiance of the laser is to be as large as possible.

2. Heavy water is a feasible solvent for rare earth chelate systems. Such systems have been obtained which display suitable solubility and characteristic rare earth fluorescence with high quantum efficiency in heavy water.

3. The photodecomposition of chelates is a major problem but obviously not one which is insoluble since europium benzoyltrifluoroacetate lases. More fundamental work is needed so that more accurate predictions can be made concerning the ability of a proposed chelate to resist photodecomposition.

4. The absorption cross section near the broad peak of the absorption band of typical chelates is too large for efficient pumping of many proposed laser systems. Some progress has already been made toward solving this problem by modifying the structure of the chelate molecule to incorporate ligands with more favorable absorption characteristics. More fundamental work in this area is, however, required.

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